Titre: Étude et mise au point d'un procédé de traitement des brasques de l'industrie de l'aluminium
Title:

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Author:

Date: 2004

Type: Mémoire ou thèse / Dissertation or Thesis

Référence: Courbariaux, Y. (2004). Étude et mise au point d'un procédé de traitement des brasques de l'industrie de l'aluminium [Thèse de doctorat, École Polytechnique de Montréal]. PolyPublie. https://publications.polymtl.ca/7439/
Citation:

URL de PolyPublie: https://publications.polymtl.ca/7439/
PolyPublie URL:

Directeurs de recherche: Jamal Chaouki, & Christophe Guy
Advisors:

Programme: Non spécifié
Program:

UNIVERSITÉ DE MONTRÉAL

ÉTUDE ET MISE AU POINT D'UN PROCÉDÉ DE TRAITEMENT DES BRASQUES DE L'INDUSTRIE DE L'ALUMINIUM

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THÈSE PRÉSENTÉE EN VUE DE L'OBTENTION
DU DIPLOME DE PHILOSOPHIAE DOCTOR
(GÉNIE CHIMIQUE)
JUIN 2004

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Your file Votre référence
ISBN: 0-612-98176-2
Our file Notre référence
ISBN: 0-612-98176-2

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Cette thèse intitulée :

ÉTUDE ET MISE AU POINT D'UN PROCÉDÉ DE TRAITEMENT DES BRASQUES DE L'INDUSTRIE DE L'ALUMINIUM

présentée par: COURBARIAUX Yann
en vue de l'obtention du diplôme de: Philosophiae Doctor
a été dûment acceptée par le jury d'examen constitué de :

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REMERCIEMENTS

J'aimerais tout d'abord adresser mes remerciements à mes directeurs de recherche: Jamal Chaouki et Christophe Guy, pour m'avoir accompagné toutes ces années. Leur ouverture d'esprit exceptionnelle m'a permis de mener à bien un projet de doctorat peu commun, qui en aurait découragé plus d'un. Leurs visions, soutiens et supports ont été des éléments essentiels de ma réussite.

J'ai une dette de reconnaissance infinie envers toute l'équipe de recherche pour leur soutien amical et leur expertise dans bien des domaines. Je pense en particulier à Pierre Sauriol, Rachid Mabrouk, Ramin Radmanesh, Eric Mc Cann, Sylvain Lefebvre, ainsi que Billy, Frédérique, Richard, Brahim, Sikun, Pierre, et tous les autres dont j'ai pu avoir oublié de mentionner le nom.

Enfin je souhaite adresser mes sincères remerciements à l'équipe de soutien de l'École Polytechnique pour m'avoir aidé à surmonter des montagnes de difficultés techniques, en particulier Gino, Jean, Robert, Carol, ainsi que Louise, Anick, Lyne, Brigitte etc… J'aimerais souligner en particulier le soutien exceptionnel de Daniel Dumas qui m'a tiré plus d'une fois d'un mauvais pas, sans rechigner et toujours avec le sourire.

RÉSUMÉ

L'aluminium résulte de la réduction de l'alumine dans une cuve d'électrolyse. Ces cuves d'électrolyse, d'une taille de plusieurs mètres utilisent des électrodes en carbone afin de conduire l'électricité nécessaire à la réaction. Après quelques années, les cathodes des cuves doivent être remplacées. Les cuves sont démolies et le déchet obtenu se nomme alors : les brasques.

Les brasques sont constituées de réfractaire (2/3) et de carbone (1/3), elles sont considérées comme des déchets dangereux car elles contiennent une forte proportion de fluors lixiviables, des cyanures et elles peuvent potentiellement contenir d'autres espèces parfois lixiviables telles que des HAPs, l'arsenic, le fer, l'aluminium etc.

Du fait de leur contenu en cyanures et fluors, les brasques sont considérées comme des déchets dangereux depuis la fin des années 80 dans la plupart des pays du monde. Elles doivent être traitées avant de pouvoir être placées en site d'enfouissement. Au Québec seulement, 50 000 tonnes de brasques sont produites annuellement et pour la majorité, s'accumulent en attente de traitement.

Le coût actuel de traitement d'une tonne de brasque est de l'ordre de 800 dollars canadiens (procédé Reynolds). Le potentiel financier a provoqué un vif intérêt de la part de groupes industriels. En conséquence, de nombreux procédés ont été mis au point de façon à traiter les brasques. Malheureusement, la plupart de ces procédés ne traitent que partiellement les problèmes de cyanures ou de fluorures, ou bien ne sont utilisables que dans des conditions particulières : les sous-produits du traitement, toujours classés comme déchets dangereux sont exploités comme matières premières pour d'autres procédés.

Par conséquent, l'objectif de ce travail est de répondre au besoin existant de développement d'un procédé simple, flexible, et efficace de traitement des brasques. Après analyse complète des études présentées dans la littérature, la solution retenue a été de séparer le traitement des cyanures de celui des fluorures afin de pouvoir conserver le maximum de flexibilité au procédé. Le procédé développé comporte trois étapes :

- La destruction des cyanures se fait par traitement thermique au lieu d'une oxydation en milieu liquide, qui est difficile dans le cas des cyanures des brasques qui sont souvent complexés par du fer.
- L'élimination des fluorures se fait par lavage en solution acide, au lieu d'être immobilisée dans une matrice vitrifiée.
- Le nettoyage de l'eau de lavage des fluorures se fait par précipitation à l'aide de calcium.

A cause des quantités d'eau habituellement requises par les procédés de lixiviation, il est prévu que l'eau de procédé puisse être recyclée, et donc l'utilisation d'une boucle de recyclage a été étudiée.

La méthodologie utilisée a été la suivante :

La destruction des cyanures a été étudiée dans un lit circulant fluidisé interne à des températures de l'ordre de 700°C à 800°C. Pour la première fois, une cinétique apparente a été obtenue. Elle est d'ordre 1 pour le carbone et permet de décrire la diminution des concentrations de cyanures dans les échantillons de petites particules étudiées. Du fait du caractère dangereux des brasques, ces données cinétiques sont très difficiles à obtenir et cela va pouvoir combler les besoins pressants émis par l'industrie. Cette étude a été l'occasion d'étudier les propriétés anti-agglomérantes d'additifs. Les résultants tendent à montrer que pour être efficace, l'additif doit être de petite taille et peut alors être utilisé dans des proportions de l'ordre de 10% ou moins dans le lit.

De plus, une cinétique apparente de dévolatilisation et de combustion des brasques a été mise au point pour la première fois. L'étude complète expérimentale, a permis de démontrer que la cinétique obtenue était libre d'interférences liées au transfert de chaleur ou de masse. Le modèle développé représente la cinétique intrinsèque de réaction des brasques. Quatre zones de réactions sont modélisées : le séchage, la dévolatilisation, une perte de masse linéaire correspondant sans doute à une réaction de coking, et enfin la combustion. L'étude a été faite à 7 valeurs du taux de chauffage, variant de 5 à 70°C/min. La mise au point du modèle a impliqué 20 mille points « fittés » simultanément. Le changement de rendement des modèles de réactions été modélisé par l'utilisation de réactions parallèles concurrentes. Un modèle de distribution d'activation d'énergie présentant des valeurs très élevées d'activation d'énergie a été utilisé pour décrire la section linéaire de pertes de masse. Les résultats obtenus sont excellents puisque toutes les variations observées sont modélisables à l'aide du même set de paramètres cinétiques pour toutes les conditions étudiées.

Le lavage des fluorures a été étudié en laboratoire avec des échantillons de petite taille. Il est démontré par XRD que seuls les sels de NaF lixivient au contraire de la cryolite. Aussi, pour des particules de petite taille, la cinétique de lixiviation des fluorures est vraisemblablement contrôlée par la vitesse de mélange et est quasi-immédiate. Un modèle basé sur une isotherme de Langmuir est utilisé pour décrire l'adsorption des fluorures dans le cas où le lavage est fait en utilisant de l'eau pure ou bien une solution concentrée de Na_2SO_4 à 120 g/L. Dans le cadre de cette étude, ce modèle est utilisé afin de définir une efficacité de lavage et ainsi de pouvoir connaître le nombre de lavages nécessaires afin de réduire la concentration de fluorures sous les normes en vigueur. Le logiciel ASPEN a été utilisé afin de mettre au point un procédé complet de traitement de lixiviation des brasques ainsi que la précipitation des fluorures par réaction avec des sels

de calcium. Une boucle de recyclage de l'eau traitée a été mise en place et utilisée afin d'obtenir les compositions des différents courants du procédé. La connaissance de la composition de ces courants a été utilisée afin de réaliser des tests qui ont permis de valider les prédictions du modèle Aspen.

Après lavage, la cryolite restante sur les brasques lixivie dans des proportions de l'ordre de 100 ppm, mesurées selon la méthode dite de TCLP. Un lavage supplémentaire à la soude permet d'éliminer la cryolite et fait descendre la lixiviation des fluorures aux alentours de 30 ppm.

En conclusion, les bases d'un procédé de traitement des brasques ont été fermement établies. Pour la première fois la cinétique de combustion des cyanures sur les particules est connue. Une cinétique apparente de dévolatilisation et combustion des brasques a été mise au point. La lixiviation des fluorures a été démontrée comme étant principalement liée à celle du NaF. Enfin, un modèle de procédé mis au point sur ASPEN a été bâti et validé.

ABSTRACT

Aluminium is the result of the reduction of alumina in electrolysis cells. These cells are of big dimensions (meters) and require the use of carbon electrodes to conduct electricity necessary for the reaction to take place. After a few years, the carbon from the electrodes must be replaced. The cells are then demolished and the waste obtained is called: Spent potliners.

Spent potliners are composed of two fractions: refractory (2/3) and carbon (1/3). They are considered an hazardous waste because they contain a high proportion of leachable fluorides, cyanides and potentially can contain other detrimental species such as PAHs, arsenide, iron, aluminum etc.

Because of their cyanide and fluoride content, spent potliners are considered a hazardous waste throughout the world since the end of the 80's. They must be treated before being landfilled. In Quebec alone, 50 000 tons of spent potliners are produced annually and presently for the most part, accumulate awaiting treatment.

The cost related to the treatment of a ton of spent potliners is about 800 Canadian dollars (Reynolds Process). The potential financial rewards lead to the development of very strong interest from the waste treatment industry. Numerous processes have been designed in order to efficiently treat spent potliners. Unfortunately, the majority of these processes only treat part of the spent potliners: either its cyanides

or fluoride content. The other processes developed can only be used in particular conditions where the hazardous by products of the treatment constitute a raw material for other industries located nearby.

Therefore, the objective of the present dissertation is to answer the existing need of development of a simple, flexible and efficient spent potliners treatment process. After completion of an exhaustive review of processes presented in the literature, the solution developed is based on the separate treatment of cyanides and fluorides in order to keep the process flexible. The process developed presents three steps :

- Cyanides removal is carried out by thermal destruction instead of liquid oxidation which is difficult when most of the cyanides present in spent potliners are iron-complexed.
- Leachable fluoride elimination is obtained by thorough fully washing the spent potliners with an acid solution instead of permanently immobilising it in vitrified matrices.
- The water used for the leaching steps is then cleaned up of its fluoride content by precipitation with calcium salts.

The process water can be potentially recycled, since the possibility of adding a recycling loop to the process has been successfully investigated.

The methodology used was the following:

Cyanides destruction was studied in an internal circulating fluidized bed at temperatures in the range 700°C to 800°C. For the first time, an apparent kinetic model of order 1 was fitted to the results in order to describe the gradual destruction of cyanides on the small particles used. This type of kinetics is particularly hard to obtain considering the hazardous nature of spent potliners, and so is really welcome by the industry. The present work was, as well, an opportunity to study the anti-agglomeration properties of various additives. Results tend to show that for the additives to have an effect, their particle size must be small, and it can then be used in proportion lower than 10% in the bed.

Fluoride's washing was studied in laboratory conditions. It was shown by using XRD tools, that only NaF salts leach in great quantity, contrarily to cryolite salts. As well, fluoride leaching kinetics were shown to be likely controlled by particles size consideration. For small size sample, leaching is quasi-immediate. A model based on Langmuir isotherm was used to described fluoride adsorption in case where washing is performed using pure water or solution of 120 g/L Na_2SO_4 salts. This model was used to define the washing efficiency of leaching in order to calculate the minimum number of washing steps necessary in order to reduce the concentration of leachable fluoride in solution below regulations. The Aspen software was used in order to design a complete process of spent potliners fluoride treatment as well as fluoride precipitation using calcium salts. A recycling loop was set up in Aspen and the predictions of the model were used to obtain the composition of the various streams in the process. The knowledge of the composition of these streams was used in order to validate the predictions of the process by performing experimental checks.

An apparent kinetic of devolatisation and combustion of spent potliners was obtained for the first time. It was demonstrated that the kinetics obtained were free of heat or mass transfer interference, so the model obtained represent the intrinsic apparent kinetics of reaction. Four zones of reaction are modeled: drying, devolatilisation, a linear weight loss zone likely related to coking, and combustion.

The study was carried out using 7 different heat ramps varying from 5 to 70°C/min. The fitting of the model involved 20 000 experimental data used simultaneously. The change of reaction yield with the heating rate observed experimentally was modelled by using a series of competing parallel reactions. A distributed activation energy model presenting very large activation energy was used to describe the linear section of weight loss. The predictions obtained are excellent, since all the variation observed are modelled using the same set of parameters for all the reactions.

After washing the remaining cryolite still leach about 100 ppm of fluoride, as tested by using the TCLP method.. An extra wash using concentrated soda, help dissolve cryolite and reduced the leaching characteristics of the residue to about 30 ppm.

In conclusion, the basis of spent potliners process was laid out firmly. For the first time, the kinetics of cyanide destruction on the spent potliners particles are known. Fluoride leaching was shown to be related to NaF salts leaching. An ASPEN model was built and validated. Finally, a spent potliner devolatilisation and combustion apparent kinetics model was obtained.

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A.E.	Activation Energy.
CH_4	Methane.
B.D.A.T.	Best Demonstrated Available Technology.
D.A.E.M.	Distributed Activation Energy Model.
E.A.	Energy d'activation.
E.P.A.	Environnemental Protection Agency (Agence de protection de l'environnement américaine
f(E)	Fonction de distribution des énergies d'activation.
$Fe(CN_6)^{4-}$	Ferrocyanures.
H_2	Hydrogène.
HAPS	Hydrocarbure Aromatiques Polycycliques (ou PAHS en anglais).
HF	Acide Hydrofluorique.
I.C.F.B.	Internal Circulating Fluidized Bed. (LFCI en français).
K088	Nom administratif des brasques pour l'E.P.A.
NaCN	Cyanure de sodium.
NaF	Fluorure de sodium.
T.C.L.P.	Toxicity characteristics leaching procedure.
T.G.A.	Thermogravimetry Analysis.
U.V.	Ultra-Violet.

CHAPITRE IV

C	Concentration en cyanures (ppm).
C_0	Concentration initiale en cyanures (ppm).
E	Energy d'Activation (kJ/mol) .
k_0	Facteur prexpoentiel (s^{-1}).
r	Rayon des particules d'additifs (m).
R	Rayon des particules de brasques (m).
s	Surface des particules de brasques occuppées par l'additif (m^2)
S	Surface des particules de brasques. (m^2)
T	Température (K).
U_0	Vitesse du gaz dans le riser (m/s).
V_p	Vitesse des particules dans le riser (m/s).
$V_{p\infty}$	Vitesse des particules dans la zone développée du riser (m/s)
z	Hauteur du riser (m)
ε	Taux de vide moyen du riser.
ε_∞	Taux de vide dans la zone développée du riser.
ρ_g	Densité du gaz (kg/m^3)
ρ_{SPL}	Densité des particules de brasques (kg/m^3)
ρ_a	Densité des particules d'additives (kg/m^3)

CHAPITRE V

$E_1,E_2,E_3,E_4,E_5,E_6,E_7$	Energie d'Activation (J/mol).
$k_1,k_2,k_3,k_4,k_5,k_6,k_7$	Facteur Preexponential (sec^{-1}).
k(T)	Constantes cinétiques dans la loi d'Arrhenius.
W	Poids normalisé de l'échantillon.
$W_{initial}$	Poids normalisé en début de réaction.
W_{final}	Poids normalisé en fin de réaction.
$W_{predicted}$	Poids normalisé prédit par le modèle durant la réaction.
$W_{unreacted}$	Poids normalisé de matériel non réagi durant la réaction.
W_{H2O}	Poids normalisé du contenu en eau de l'échantillon.
$n_1,n_2,n_3,n_4,n_5,n_6,n_7$	Ordre de réaction.
Ni	Nombre total de points dans les expériences où les taux de chauffage sont variés.
R	Constante de gaz idéale [J/(mol.K)]
T	Temps (Second).
T	Température (Kelvin).
X	Conversion.

Lettres Grecques :

α	Fonction. Objective
B	Taux de chauffage (Celsius/Second).

CHAPITRE VI et VII

E	Efficacité de lavage.
K	Intensité d'adsorption de l'isotherme (g/L).
W_{max}	Charge maximum de fluorures en g par g de brasques.
X_0	Fraction dissous des sels dans le courant d'entrée.
X_{out}^{L}	Fraction dissous des sels dans le courant liquide de sortie.
X_{out}^{S}	Fraction dissous des sels dans le courant solide de sortie.

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INTRODUCTION

L'industrie de l'aluminium est une industrie clé du Québec qui abrite le siège sociale de la plus importante aluminerie au monde: La compagnie Alcan. L'aluminium résulte de la réduction de l'alumine dans une cuve d'électrolyse. Alors que les mines d'alumine sont situées ailleurs à l'étranger, les bas coûts en électricité du Québec ont permis l'implantation de nombreuses usines de réduction de l'alumine. Les cuves d'électrolyse utilisées lors de cette réduction sont massives et présentent une taille de plusieurs mètres. Elles sont construites autour d'électrodes de carbone qui permettent de conduire l'électricité nécessaire à la réaction de réduction. Après quelques années, les cathodes en carbone des cuves doivent être remplacées alors que l'anode est consommée au cours de la réaction de réduction. Les cuves sont alors démolies et le déchet obtenu, composé du réfractaire des parois des cuves ainsi que des cathodes de carbone se nomme alors : les brasques.

Les brasques sont un déchet dont la disposition présente de nombreux problèmes environnementaux. Elles sont considérées comme des déchets dangereux car elles contiennent une forte proportion de fluors lixiviables, des cyanures et elles peuvent potentiellement contenir d'autres espèces parfois lixiviables telles que des HAPs, de l'arsenic, du fer, de l'aluminium etc. Elles sont à d'ailleurs l'origine d'un accident mortel au Québec impliquant le chargement de brasques à des fins d'expédition dans un pays en voie de développement. Une atmosphère réactive composée de méthane et d'hydrogène a été générée par la réaction des brasques avec l'eau résiduelle des cales, ce qui a mené à l'explosion meurtrière.

Du fait surtout de leur contenu en cyanures et fluors, les brasques sont considérées un déchet dangereux depuis la fin des années 80 dans la plupart des pays du monde. Elles doivent être traitées avant de pouvoir être placées en site d'enfouissement ou bien recyclées. Au Québec seulement, 50 000 tonnes de brasques sont produites annuellement et pour la majorité, s'accumulent en attente de traitement. Alcan a fait construire des entrepôts spécialisés près de ses usines de lac St Jean afin de pouvoir stocker le demi million de tonnes de déchets en attente de traitement. Cependant la volonté politique du gouvernement Québécois ces dernières années impose aux producteurs d'aluminium l'obligation de s'attaquer à ces importantes accumulations.

En conséquence, les brasques sont un type de déchet dangereux soulevant un intérêt prononcé de la part de plusieurs industriels. Cependant aucun procédé, à date, n'est reconnu comme étant suffisamment efficace pour s'imposer comme solutions aux producteurs d'aluminium. Cette thèse s'inscrit dans le cadre du développement d'un procédé de traitement des cyanures et fluorures des brasques.

CHAPITRE I :

REVUE DE LA LITTÉRATURE

1.1 Contexte industriel du projet : L'industrie de l'aluminium

L'aluminium représente 7.3% de la composition de la croûte terrestre. C'est donc un composé très répandu sur Terre. Cependant, il ne peut être trouvé dans la nature sous forme pure, mais seulement sous la forme d'oxyde.

Deux procédés permettent d'obtenir le métal aluminium et de le mettre en forme :

- Le procédé dit de première fusion, qui génère de l'aluminium métallique à partir de bauxite,
- Le procédé dit de deuxième fusion qui correspond à l'utilisation de l'aluminium recyclé.

Seul le procédé de première fusion génère des brasques et constitue donc un intérêt dans le cadre de cette thèse.

Tous les procédés de fabrication de l'aluminium comportent des variantes, mais sont fondamentalement constitués de 3 étapes :

- Extraction du minerai (bauxite).
- Extraction de l'alumine (Al_2O_3) du minerai par un traitement chimique.
- Électrolyse de l'alumine afin de réduire l'oxyde en aluminium.

L'étape d'extraction de l'alumine de la bauxite, se fait à l'aide de lavages basiques dans un bain de soude. Cette extraction génère des quantités importantes de déchets basiques et de résidus nommés 'boues rouges'. L'alumine passée en solution, est ensuite précipitée et récupérée par filtration.

L'étape de réduction des cristaux d'alumine récupérés en aluminium a lieu dans une cuve d'électrolyse. Les premiers à avoir mis au point ce procédé sont le français Paul Héroult et l'américain Charles Hall au début du 20ème siècle. Le procédé utilisé aujourd'hui porte leurs deux noms soit le procédé Hall Héroult.

Le réacteur d'électrolyse est constitué d'une cuve remplie d'alumine et de cryolite fondue pouvant mesurer de 1 à 1.5 mètres de hauteur, 5 à 15 mètres de longueur et 3 à 5 mètres de largeur (voir figure 1.1) (Chanania et Eby, 2000). Il contient une cathode, une anode, et des cristaux d'alumine dissous dans un bain très corrosif de cryolite (Na_3AlF_6) à haute température. Le courant servant à lors de l'électrolyse circule par l'intermédiaire de barres d'acier insérées dans la cathode. Le contenu corrosif du bain peut attaquer ces barres, il est donc important d'empêcher le contact direct. C'est pour cela que des cathodes en carbone, très résistantes à la corrosion et conductrices d'électricité sont utilisées comme enrobage protecteur tout en permettant un bon contact électrique.

Même si l'alumine est liquide vers 2040°C, un mélange constitué de 81.5% de cryolite et de 18.5% d'alumine constitue un eutectique qui fond à environ 950°C. Ce mélange permet d'obtenir un bain d'alumine liquide à des températures plus basses et donc à un coût réduit. En plus de ces composés, d'autres additifs sont ajoutés au bain en proportions importantes afin d'améliorer la consommation énergétique et le fonctionnement du procédé : fluorures d'alumine, fluorures de sodium, soude, fluorures de calcium, carbonate de lithium, et oxyde de magnésium (Silveira et al., 2002)

La matière première du bain : la cryolite, est préparée par la réaction du fluorspar avec des sels de fluorures de sodium ou par réaction de la soude avec de l'alumine en présence d'acide fluorhydrique.

$$3NaF + AlF_3 \rightarrow Na_3AlF_6 \qquad (1a)$$

$$6NaOH + Al_2O_3 + 12HF \rightarrow 2Na_3AlF_6 + H_2 \qquad (1b)$$

Dans le bain, les réactions ayant lieu sont très complexes et mal connues. Cependant, il est possible de résumer les réactions ayant lieu par la réaction globale suivante (Chanania et al. 2000) :

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2 \qquad (2)$$

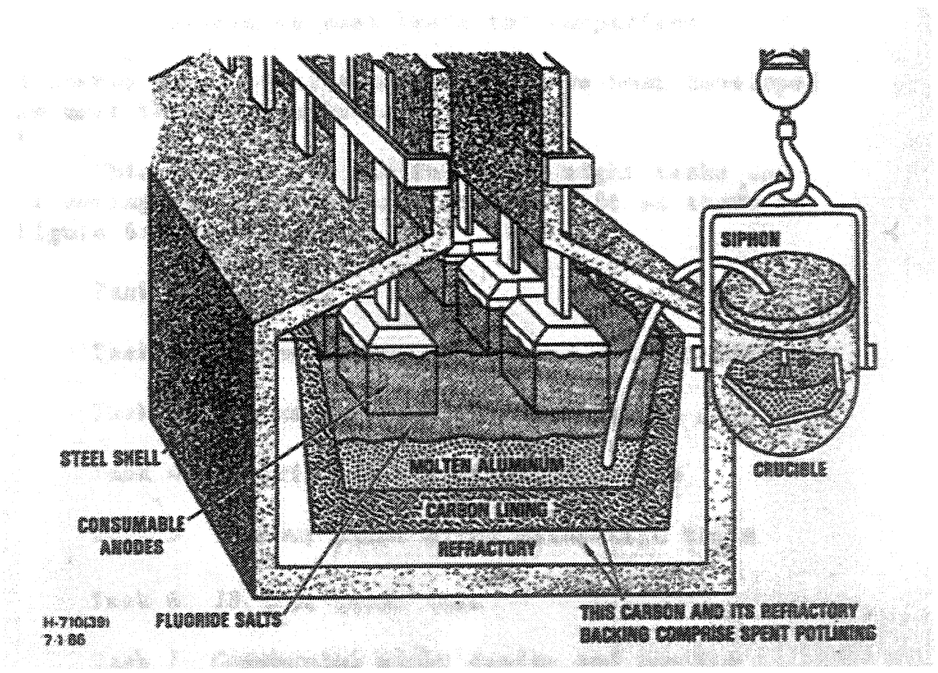

Figure 1.1 : Cuve d'électrolyse (d'après Rickman et al., 1993)

Lors de l'électrolyse un courant électrique est imposé entre anode et cathode. L'alumine est alors réduite en aluminium à la cathode. L'aluminium réduit et fondu s'accumule au fond de la cuve et doit être retiré. C'est un procédé de type batch puisque régulièrement les cuves sont vidées afin de retirer le bain et d'en récupérer l'aluminium.

L'anode est constituée de carbone, qui est consommé lors de la réaction. Elle doit être remplacée tous les 20 à 30 jours. Cette anode est suspendue au-dessus de la cuve et trempe dans le bain de cryolite.

La cathode est aussi constituée de carbone et recouvre tout le fond du réacteur. De façon à l'isoler thermiquement, une couche de réfractaire se trouve en dessous de cette couche de carbone. La durée de vie des cathodes est d'environ trois à huit ans selon Alcan (2002) ou Brooks et al (1991).

1.2 La problématique des brasques :

1.2.1 Génération

Du fait de l'atmosphère réductrice présente au dessus du bain, l'azote de l'air est susceptible de réagir avec le carbone de la cathode pour former un ensemble d'espèces chimiques dont des nitrures et cyanures (Pawlek, 1993, 1997; Silviera et al., 2002). De plus à ces hautes températures, la formation de HAPS à l'intérieur des électrodes est possible. Enfin, sous l'effet combiné du vieillissement et des hautes températures l'aluminium fondu, le sodium, les fluorures de calcium et l'alumine s'infiltrent dans la cathode. Les variations de températures ainsi que la cristallisation des espèces infiltrées se traduisent par des tensions mécaniques qui fragmentent la cathode. (Bontron et al. 1992)

De plus, certaines réactions chimiques peuvent survenir entre l'aluminium (ou le calcium) et le carbone pour produire du carbure d'aluminium (ou de calcium). En fin de vie, la cathode fracturée et la couche de réfractaire qui lui est attachée, doivent être retirées et éliminées. Ce déchet se nomme : la 'Brasque'.

Le Canada est le troisième plus grand producteur mondial d'aluminium primaire derrière les États-unis et la Russie. Annuellement, 2.3 millions de tonnes métriques d'aluminium y sont produits. Les principaux producteurs canadiens sont Alcan Aluminium Limitée, la société canadienne Reynolds Limitée et depuis 1986 Aluminerie de Bécancour Inc., Aluminerie Lauraclo inc., Alouette. Le Québec joue un rôle très important dans cette capacité de production puisqu'il est à l'origine de la production de 2 millions de tonnes métriques annuellement. Sur les douze alumineries du Canada, onze sont au Québec et une en Colombie Britannique. En 1998, l'industrie de l'aluminium générait annuellement 5.7 milliards de dollars d'exportation et permettait de créer 13000 emplois directs et 6000 emplois indirects aux États-unis. Les États-unis dénombrent 23 alumineries dont la production totale d'aluminium est de 3.6 millions de tonnes (Paradis et al.,1998)

Cette production d'aluminium se traduit par la génération d'énormes quantités de déchets dont les brasques. Au niveau mondial, il est estimé que de 800 000 à 1 million de tonnes de brasques sont générées annuellement. La quantité de brasques générée dépend des producteurs d'aluminium et de leurs objectifs de réduction mais est estimée à environ 80 000 à 120 000 tonnes par an aux U.SA. (Chanania et al., 2000). Selon Pechiney cette quantité est de l'ordre de 13 à 15 kg par tonne d'aluminium produite (Bronton et al. 1992), alors que selon l'EPA (EPA, 1996) cette quantité est de l'ordre de 26 kg par tonne d'aluminium produit. En général, la production d'une tonne d'aluminium implique la génération de 13 à 50 kg de brasques usées (Pawlek, 1993, Kimmerle et al., 1994). Ainsi, 17 % de la production de brasque annuelle est stockée en attente de traitement, 61 % est enfouie, et la différence subit une forme de traitement.

Les brasques usées sont composées en moyenne d'environ 2/3 de carbone et 1/3 de matériaux réfractaires mais présentent une composition très variable (voir table 1.1).

En 1993, Pawlek (1993) estimait que le traitement d'une tonne de brasques reviendrait en moyenne à 1000 $ la tonne aux États-unis. Cette estimation démontre l'importance économique sociale et politique du problème des brasques.

1.2.2 Risques pour la santé

Les brasques constituent un risque pour la santé principalement lorsqu'elles sont mises en contact avec des composés à hydrogène labile. En rentrant en contact avec de l'eau, ou des espèces acides, les espèces réductrices présentes dans la brasque peuvent réagir afin de générer plusieurs types de gaz dont de l'ammoniac, de l'hydrogène et du méthane. Si ces gaz ne sont pas évacués alors ils peuvent s'accumuler et provoquer une explosion. (Brooks et al., 1991).

De plus, les brasques, en contact avec de l'eau lixivient de nombreuses espèces, dont des fluorures. (Yap, 1993; Peterson et al, 1993).

Enfin sous l'effet de hautes températures, les brasques sont susceptibles de subir une dévolatilisation qui permet d'émettre des fluorures, mais aussi des cyanures d'hydrogène.

1.2.3 Les cyanures et les fluorures des brasques.

Les cyanures sont principalement trouvés dans les zones les plus froides de la cathode. La concentration locale varie selon les endroits entre 0.6 et 1 % du contenu total en brasques. Ils sont issus de la réaction de l'azote de l'air avec le carbone en atmosphère réductrice. Lors de leur stockage, le cyanure de sodium réagit avec l'humidité et la rouille pour former des ferrocyanures (Kimmerle et al., 1994).

À terme, les cyanures contenus dans les brasques sont de deux types principalement des ferrocyanures, et du cyanure de sodium (Fortin et al, 2000). Si le cyanure de sodium est relativement facile à traiter du fait de sa solubilité, les ferrocyanures constituent une source de polluants très toxiques, difficile à traiter.

Les fluorures dans les brasques se trouvent initialement sous la forme de NaF et sont principalement issus des réactions suivantes ayant lieu dans la cuve (Balgord, 1978) :

$$\begin{aligned} &4Na_3AlF_6 + 12Na + 3C \rightarrow Al_4C_3 + 24NaF \\ &4Na_3AlF_6 + 6Na_2O \rightarrow 2Al_2O_3 + 24NaF \end{aligned} \qquad \text{(3 et 4)}$$

Une proportion significative de fluorures se retrouve aussi sous forme de cryolite.

1.3 Législation concernant les brasques :

Selon le règlement sur les matières dangereuses (Q-2, R.15.2), les brasques sont considérées comme matière dangereuse au Québec depuis septembre 1985. La Loi sur la qualité de l'environnement, section 70.1 à 70.9 précise les conditions d'entreposage et de manipulation des brasques. À peu près 50 000 tonnes de brasques usées sont générées au Québec annuellement (Alcan 2002). Près de la moitié de ce tonnage provient des usines d'Alcan. Depuis 1980, Alcan a entreposé près de 500 000 tonnes de brasques, en attendant de trouver une solution pour les traiter.

Tableau 1.1: Composition moyenne des brasques selon références.

Composition des brasques (en %)	**Paradis et al.1998**	**Brooks et al. 1992**		**Bontron, 1992**	**Reynolds 1996**	**Alcan 1997**	**EPA 1996**	**Brown and Reddy (1994)**	**Pawlek, 1993**	**Kidd, 1993**	**Ogden (1984) Reynolds**	**Ogden (1984) Alcan**
Aluminium	5.4	20.4	20.4	3-8	5-22	5.4	4-6	11.0	7-22	22.8-7.9	5	14
Briques réfractaires	42.8					42.8						
Réactifs	0.2											
Carbone	23.5	24.8	16.9	25-55	10-50	23.5	50	25.0	13-69	9.6-57.5	43	29
Sodium	14.8	19.5	19.4	12-19	7-20	14.8	10-18	15.5	9-22	8.8-14.2	20	14
Cyanures	0.1			0.1	0.02 - 0.44	0.1	0.5	0.15	0.002-0.6	0.1-0.7	0.14	0.1
Fluorures	13.2	17.9	21.3	6-10	6-19	13.2	10-15	16.8	7-22	13.5-15.0	18	18
HAPs				-	-		<0.1				-	-
Phénols				-	-		<0.1				-	-
Réactifs				-		0.2	-				-	-
Silice		0.79	0.03	<15				4.53	1-11	8.5-2.0	0.1	5
Calcium		2.26	2.0	1-2	1-3		1-3	2.54	1-2.6	1.9-1.3		
Fer		0.69	0.54	0-2	0-2		0-1		0.3-0.8	0.8-0.4		

Aux États-Unis, depuis septembre 1988, L'EPA considère la fraction carbonée comme étant un déchet dangereux (53 Fed. Reg. 35412). Les brasques sont connues sous le nom de K088 dans la législation américaine. Elles ne peuvent être enfouies sans traitement préalable. Cependant la partie réfractaire des brasques ne constitue pas un déchet dangereux et peut être réutilisée sans traitement. (Goldman, 1987,1990)

L'EPA considère les brasques comme étant dangereuses du fait principalement de leur contenu en cyanures et en fluorures, mais aussi de leur contenu en HAPs et métaux lourds (arsenic…) (Chanania et al, 2000)

Seules deux compagnies nord-américaines acceptent de traiter les brasques :

- Reynolds est la seule compagnie, sur le continent américain, offrant un procédé de traitement des brasques acceptant de prendre en charge les brasques de ses concurrents. Ce procédé permet de générer des cendres qui en 1996 ont été déclassées et considérées comme déchet non dangereux. Cependant en 1997, il est apparu que la technologie ne remplissait pas ses promesses. Les déchets obtenus par le traitement étant fortement alcalins, la lixiviation des fluorures était renforcée dans les conditions naturelles, non prédites par les tests de TCLP traditionnels. Le déchet a alors été reclassé déchet dangereux du fait du non-respect de la législation. (The Hazardous Waste Consultant, 1999).

- Ormet dispose d'une technologie de traitement des brasques très au point qui a été déclarée BDAT (Best Demonstrated Available Technology) par l'E.P.A. en 2000 (Chanania et al. 2000). Cependant, ce traitement ne semble pas accessible à ses concurrents.

1.4 Méthodes de traitement et revue de littérature :

Plusieurs types de traitements existent et sont généralement classés en trois grandes familles :

- Procédé hydro métallurgique avec méthode de lixiviation à basse température.
- Procédé thermique à température modérée.
- Procédé pyrométallurgique par lequel, on fond littéralement la matière avec comme résultat l'obtention d'un produit liquéfié.

La qualité d'un bon procédé de traitement des brasques va être définie selon plusieurs critères : (Jeppet et al. 1996) :

- Faisabilité technique.
- Faibles coûts d'investissement et d'opération.
- Conformité aux exigences réglementaires en matières d'environnement.
- Tolérance pour des variations dans le matériel à traiter.
- Génération de résidus secondaires. Idéalement aucun déchet dangereux ne devrait être généré par la technologie.
- Maximiser la récupération des composantes recyclables.
- Possibilité de manufacturer des produits de recyclages utiles.

La revue des technologies de la littérature ouverte a permis d'identifier les applications commerciales suivantes :

- Le LCLL développé par Alcan. (Canada)
- Le procédé LIPPEWERK : Production de cryolite (Allemagne)
- Procédé de vitrification Vortec de la compagnie ORMET. (U.S.A)
- Procédé de REYNOLDS, Arkansas. (U.S.A)
- Procédé COMTOR (Canada)
- Procédé pyrométallurgique AUSMELT (Australie)
- Procédé SPLIT de Péchiney (France).

Chaque technologie ainsi que les techniques de recyclages sont décrites en détail en Annexe A. Le tableau 1.2 résume les caractéristiques des différents procédés.

Les procédés sont séparés en deux catégories : stade industriel ou non démontré. Puis en sous-catégories : Procédé de lavage, hautes températures, très hautes températures et avec maximisation du recyclage ou stabilisation des résidus. Les conditions de traitements des cyanures ou fluorures y sont résumées.

Tableau 1.2: Résumé des procédés de traitement des brasques

PROCÈDÉ	Taille particules (mm)	Traitement des **cyanures**			Traitement du **fluor**	Coûts US $/tonne	
		Action	Temps de résidence	Température			
PROCÉDÉS AU STADE INDUSTRIEL							
Procédé de **LAVAGE** avec pour but la maximisation du **RECYCLAGE** des matériaux.							
Alcan	<0.5	3 lixiviations basiques puis hydrolyse en réacteurs chauffés à la vapeur d'eau.	Environ une heure	182 et 1.5 MPa de pression.	Précipitation de NaF par évaporation.	91 Millions Investissements	Recyclage complet des brasques
Lippewerk	0.1	Lixiviation basique à 80°C puis destruction par UV	3 à 4 heures	N/D	NaF recyclé dans la production de cryolite	333 $	Plus en opération, pas de marchés pour les produits recyclés.
Procédé à **TRES HAUTES** températures avec **MAXIMISATION** du recyclage des matériaux.							

Ormet	0.4	Oxydation en réacteur Vortec.	N/D	1200 à 1500	Vitrifié ou récupéré dans la cheminée sous forme de HF et fixé par de l'alumine pour la production de fluorspar. Résidu utilisé pour la fabrication de carrelage.		Déclarée BDAT par l'EPA
Ausmelt	25.4	Oxydation en bain de scories fondues	N/D	1300	Vitrifié ou récupéré dans la cheminée sous forme de HF et fixée par de l'alumine sous forme de fluorspar, revendable.	186 $	Une partie des résidus sont censés être revendus.
Procédés à **HAUTES** températures avec **STABILISATION** des brasques à des fins d'enfouissement							

Reynolds	50	Oxydation en four rotatif	90 minutes	540 à 760	Fixé en CaF_2 lors de la combustion	400 $	Les résidus obtenus sont toujours classés déchets dangereux .
Comalco	1	Oxydation en Torbed sans combustion du carbone.	N/D	550 à 700	Fixée en CaF_2 après lavage basique.		En opération en Ontario.
Procédés à **HAUTES** températures avec **STABILISATION** des brasques à des fins d'enfouissement.							
SPLIT	2.5	Oxydation en réacteur Vortex. Un additif (sulfate de calcium) est utilisé pour fixer le fluor.	5 secondes	1100 à 1800°C	Fixé sous forme insoluble lors du chauffage (CaF_2)		

<table>
<tr><th colspan="8">PROCÉDÉS INCOMPLETS OU NON-DEMONTRÉS.</th></tr>
<tr><td colspan="8">Procédé de LAVAGE avec pour but la MAXIMISATION du recyclage des matériaux.</td></tr>
<tr><td>Deutschman</td><td>20</td><td>Les cyanures sont détruits par l’utilisation d’un petit four rotatif.</td><td>48 minutes (insuffisant)</td><td>350°C</td><td>Lixiviation à l’eau puis à l’acide sulfurique et chaux, fluorures précipités.</td><td>100 $</td><td></td></tr>
<tr><td>Blayden</td><td>10</td><td>Lixiviations successives et batch dans l’eau (2 heures)</td><td>Réaction avec l’hypochlorite de sodium</td><td>N/D</td><td>Précipité sous forme de CaF_2</td><td></td><td></td></tr>
<tr><td>Gnyra</td><td>0.2</td><td>N/D</td><td>N/D</td><td>N/D</td><td>De l’acide sulfurique permet l’émission de HF utilisé dans la synthèse de AlF_3. L’acide sulfurique est recyclé par carbonisation de Na_2SO_4</td><td></td><td>Procédé permettant le recyclage du fluor.</td></tr>
</table>

Bush	0.1	Lavage basique puis acide. Les cyanures sont transformés en volatiles et sont oxydés.	N/D	N/D	NaF est élimée par réaction avec $Al(OH)_3$ pour former du AlF_3 L'acide sulfurique du procédé et la soude sont régénérées par électrolyse.	2767 $	Procédé coûteux et complexe.
Pong	-	Lavage eau et précipitation avec zinc, puis oxydation.	N/D	N/D	Précipitation en CaF_2	100-200	
Procédés à **TRES HAUTES** températures avec **STABILISATION** des brasques à des fins d'enfouissement.							

Ogden	60	Oxydation en lit fluidisé		800 C.	Non traité		Procédé en lit fluidisé circulant. Pas d'agglomération, cyanures détruits, mais les fluorures lixivient.

Divine	1	Oxydation avec vapeur d'eau		800 C	Non traité.		Gazéification des brasques, le gaz obtenu serait commercialisable.
Procédé à **HAUTES** températures avec **MAXIMISATION** du recyclage des matériaux.							
Elkem	15	Oxydation en bain fondu	N/D	N/D	Les fluorures sont vitrifiés. Ils peuvent être aussi éliminés sous la forme de HF en utilisant de la vapeur d'eau sur le bain fondu.	200	Utilisation de brasques comme agent réducteur dans la production d'acier

1.5 Conclusion de la revue technologique :

En ce qui concerne le traitement des cyanures, le stade industriel a été atteint par :

- 2 procédés basés sur un traitement à basse température (lixiviation).
- 2 procédés basés sur un traitement à température moyenne (combustion).
- 3 procédés basés sur un traitement à très hautes température (vitrification).

En ce qui concerne le traitement des fluorures, le stade industriel a été atteint par :

- 2 procédés basés sur le recyclage de NaF.
- 2 procédés basés sur le recyclage de fluor sous la forme de AlF_3 par l'intermédiaire de HF.
- 3 procédés basés sur la stabilisation en CaF_2

Les options technologiques et les rapports de développement ne manquent donc pas sur le sujet de traitement des brasques. Cependant aucune option technologique n'est reconnue comme étant supérieure aux autres par la majorité des alumineries. La plupart du temps, c'est une question de coûts. Les procédés ont été développés en fonction d'alumineries et d'installations présentes localement et sont difficilement adaptables à d'autres localisations, le recyclage de matières premières n'étant souvent plus possible. Cela rend la plupart des procédés inintéressants du point de vue économique, sauf exception.

Comme la revue de littérature l'aura souligné, une vaste gamme de procédés a été développée à ce jour pour le traitement des brasques. Malheureusement, la plupart des études sur le sujet se sont limitées à des tests au niveau industriel de nouvelles technologies, sans approfondir les résultats obtenus.

De plus, les industriels québécois contactés sur le sujet, confirment leurs frustrations par rapport à ces nouvelles technologies. Toutes les brasques et usines de production d'aluminium sont différentes. Si certaines technologies de traitement impliquant un haut taux de recyclage sont faciles à implanter sur le site de certaines usines du fait de la présence de cimenterie, ou usines de production d'acier etc. aucune d'entre elles n'est suffisamment flexible pour s'imposer comme une solution unique (Wellwood, et al., 1993; Brooks et al, 1991)

Par conséquent, il est important de développer un nouveau procédé qui soit flexible, simple d'utilisation, économique et étudiable du point de vue scientifique en utilisant des sources provenant de la littérature ouverte. Cette nouvelle technologie implique :

- Un traitement séparé des cyanures et fluorures pour garder le maximum de flexibilité au point de vue du procédé.

- Le traitement doit se faire à l'aide de technologies simples et reconnues. Par conséquent, les cyanures seront traités par combustion, et les fluorures par lixiviation.

- La minimisation des coûts passe par l'utilisation de procédés qui ne visent pas le recyclage immédiat des produits issus de la dégradation des brasques. Les marchés industriels sont très réticents à utiliser des produits issus du traitement de déchets dangereux. Cependant dans le design du procédé, la possibilité du recyclage devra être considérée afin d'améliorer l'aspect économique du procédé.

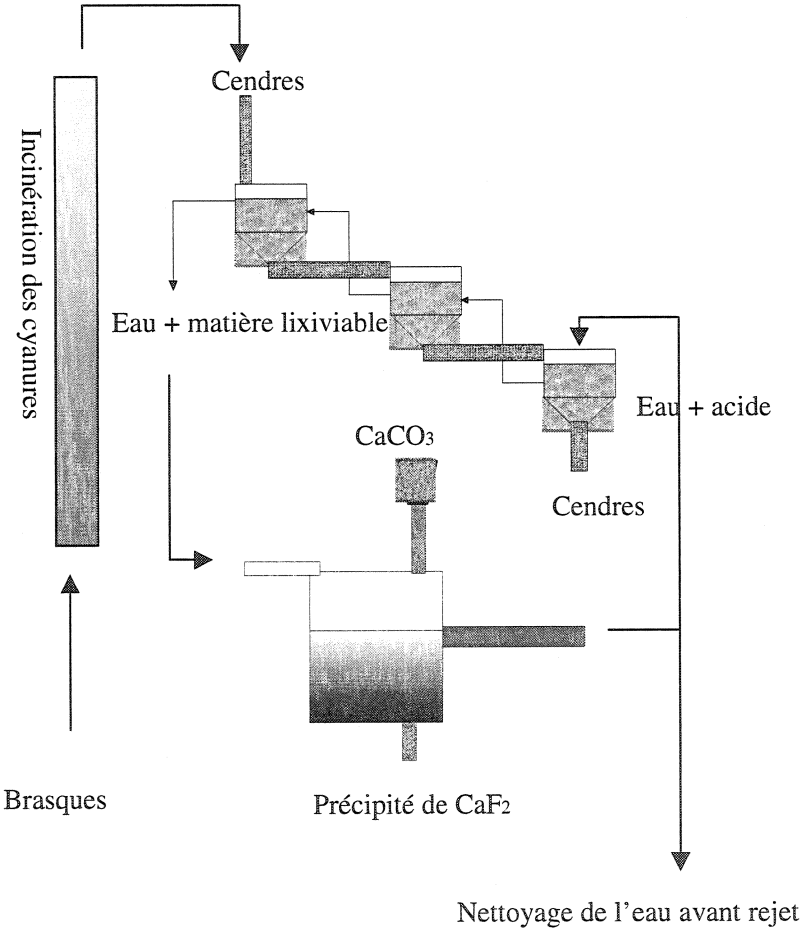

Figure 1.2 : Description du procédé développé.

Par conséquent le procédé développé comporte trois étapes :

1) Destruction des cyanures par incinération dans un lit circulant fluidisé.

2) Élimination des fluorures en CaF_2, potentiellement recyclable, par lavages successifs (figure1.2).

3) Traitement de l'eau de procédé issue des étapes du lavage.

CHAPITRE II

PRÉSENTATION DES ÉTAPES DE TRAVAIL

Cette section décrit l'organisation générale des principales étapes du travail qui ont fait l'objet de cette thèse.

Précisons tout d'abord que l'objectif principal de recherche était: 'Le développement d'un procédé simple, économique et flexible pour le traitement du contenu en cyanures et fluorures des brasques.'

Dans le cadre de la réalisation de cet objectif, les sous objectifs suivants ont été atteints :

1) Mesurer et modéliser la cinétique de destruction des cyanures par traitement thermique.
2) Mesurer et modéliser la cinétique de dévolatilisation et de combustion des brasques.
3) Mesurer, modéliser et optimiser la lixiviation contrôlée du fluor des brasques en fluorure de calcium.

Le chapitre 3 décrit brièvement la méthodologie utilisée pour atteindre les objectifs tels que définis précédemment. La suite de la thèse comprend quatre articles, présentés sous la forme de quatre chapitres.

Le premier article ou chapitre 4, est intitulé '*Update on Spent Potliners treatments : Kinetics of Cyanides destruction at High Temperature*' et a été accepté pour publication dans la revue I&ECR. Il traite de la destruction des cyanures dans un lit circulant fluidisé interne, ainsi que des problèmes d'agglomération. Grâce aux résultats expérimentaux obtenus, un modèle cinétique de destruction des cyanures est mis au point. Un mécanisme d'action d'additifs anti-agglomération est aussi suggéré. Les résultats démontrent qu'il est possible de procéder à la destruction des cyanures dans des conditions contrôlées de combustion.

Le chapitre 5 est constitué de l'article intitulé '*Modeling of Spent potliners Devolatilisation and Combustion by Thermogravimetry Analysis*' soumis pour publication dans la revue *Fuel.* Cet article décrit la mise au point d'un modèle complexe et exhaustif de combustion et dévolatilisation des braques, à partir de données obtenues par thermogravimétrie. Ces données sont essentielles lors du traitement thermique des brasques afin de pouvoir évaluer la proportion de carbone brûlée lors de la destruction des cyanures et ainsi contrôler la température de l'unité de combustion et diminuer les risques d'agglomération. À partir des résultats du chapitre 4 et 5, il est facile de procéder à la destruction des cyanures tout en contrôlant la combustion des brasques.

Le reste de la thèse porte sur le traitement des fluorures des brasques. Le chapitre 6 est constitué de l'article intitulé '*Spent potliner fluoride adsorption characterisation*' soumis pour publication dans la revue *Separation and Purification Technology.* Il décrit l'obtention de résultats expérimentaux de lixiviation des fluorures des brasques, ainsi que la mise au point d'un modèle d'adsorption des fluorures sur les brasques. Les résultats obtenus sont utilisés afin de déterminer les paramétres d'un modèle de Langmuir permettant de décrire l'adsorption des fluorures obtenues. L'étude est faite en utilisant deux solvants afin de vérifier les effets possibles du recyclage de l'eau lors du procédé décrit au chapitre suivant.

Le modèle de lixiviation est utilisé au chapitre 7 afin de mettre au point un procédé de traitement des fluorures des brasques par lixiviation à l'aide du logiciel Aspen. Ce modèle est ensuite validé dans les étapes clés par des résultats expérimentaux. Le chapitre 7 est constitué par un article soumis à la revue '*Journal of Hazardous Material*' et est intitulé '*Development and validation of a leaching process of the spent potliner fluoride content*'. Il comporte la particularité de recycler l'eau de procédé et d'être très flexible, permettant ainsi une optimisation des étapes selon le type de brasques traitées

CHAPITRE III :

MÉTHODOLOGIE

Ce chapitre décrit les principales méthodes utilisées pour mener les expériences et générer les données.

3.1 Caractérisation des brasques utilisées dans cette étude.

Toutes les brasques sont différentes les unes des autres. Leurs caractéristiques varient selon l'aluminerie, l'année de production etc… (Byers, 1986). Par contre, elles présentent toutes des caractéristiques communes (concentration de fluorures, cyanures, réfractaires, carbones).

Au cours de ce projet, deux types de brasques sont étudiés :

- Les brasques d'Alouette, aluminerie située à Baie Comeau sur la côte Nord.
- Des brasques issues des alumineries d'Alcan à Jonquière.

Ces brasques nous ont été livrées en provenance des alumineries déjà broyées à moins de 2 mm. La taille moyenne des deux brasques est de l'ordre de 500 µm.

Tableau 3.1 : Composition des brasques fraîches utilisées dans cette étude.

Composition	**Alcan**	**Alouette**
Carbone	20-35 %	<14 %
Sels de fluor	15.4 %	14 %
Cyanures	0.046 %	0.038 %
Sodium	15.6 %	14.2 %
Aluminium	9.8 %	13 %

Les brasques d'Alouette ont été utilisées pour procéder aux essais de combustion et de destruction des cyanures. La principale raison de ce choix était que les brasques d'Alouette présentent un contenu énergétique plus faible que celles d'Alcan (14 % contre 30 % en moyenne), ce qui facilite le contrôle de température dans l'unité de combustion.

Même si les brasques d'Alouette ont été les seules dont la combustion fut testée en détail sur l'unité pilote de combustion, quelques essais de combustion ont tout de même été menés avec les brasques d'Alcan, prouvant que la fluidisation est possible et que l'agglomération n'a pas eu lieu.

Par contre, seules les brasques d'Alcan ont été utilisées dans le cadre des essais de lixiviation, principalement parce que les brasques d'Alcan ont une proportion de fluorures lixiviables plus importante que celles d'Alouette et les brasques envoyées par d'Alcan sont reconnues comme étant particulièrement difficiles à lixivier.

3.2 Mesurer et modéliser la cinétique de destruction des cyanures par traitement thermique.

La cinétique de destruction des cyanures est particulièrement difficile à obtenir du fait du caractère dangereux des brasques, du fait que d'autres espèces sont susceptibles d'être brûlées en même temps, et du fait de la sensibilité de cyanures à la dégradation thermique. Cette cinétique a été déterminée en brûlant partiellement les brasques dans un lit circulant fluidisé interne. Ce lit circulant fluidisé interne permet de traiter plus d'une centaine de kilos de matériaux combustibles et a été complètement modélisé par Mukadi et al. (1998).

Les critères étudiés lors de la combustion ont été :

a) Identification d'un adjuvant permettant d'empêcher l'agglomération, ainsi que de trouver les proportions optimales d'adjuvant pour que les expériences puissent avoir lieu.

b) Détruire le cyanure : Vérifier la destruction des cyanures et modéliser la cinétique de destruction des cyanures.

c) Déterminer les conditions permettant de limiter les émissions de HF.

3.3 Mesurer et modéliser la cinétique de dévolatilisation et de combustion des brasques.

Ces données sont essentielles afin de bien contrôler le procédé de destruction thermique des cyanures. Elles ont été obtenues à l'aide d'une balance thermogravimétrique: 'Mettler Toledo'. Les expériences ont été faites en ayant pour objectifs :

- Modéliser les réactions chimiques intrinsèques. Cela implique la minimisation des effets du transfert de chaleur et de masse lors des réactions.
- Obtenir un modèle particulièrement robuste, valide quelle que soit la rampe de chaleur utilisée, ce qui implique des paramètres fittés de réaction, indépendants des conditions expérimentales.

Une description complète de l'utilisation d'une balance thermogravimétrique peut être trouvée en annexe.

L'optimisation du modèle mathématique été réalisée à l'aide du logiciel Matlab, en ayant pour objectif de minimiser la valeur de la fonction objective :

$$\alpha = \sum_{i=1}^{K} \sum_{j=1}^{N_i} \frac{\left| W_{predicted} - W_{measured} \right|}{N_i} \qquad (1)$$

Où K représente le nombre de points expérimentaux pour l'expérience faite, N_i est le nombre total de points pour cette expérience. Cette fonction objective a été choisie de cette forme car l'obtention d'une évaluation de l'erreur entre le modèle et les prédictions expérimentales est directe.

Le choix du mécanisme expérimental a été fait en utilisant des modèles cinétiques décrits dans la littérature et en les complexifiant jusqu'à ce que toutes les tendances obtenues expérimentalement puissent être prédites par le modèle.

3.4 Mesurer, modéliser et optimiser la lixiviation contrôlée du fluor des brasques en fluorure de calcium.

La lixiviation des fluorures des brasques a été étudiée par l'intermédiaire d'expériences de lavage batch en laboratoire et dans des conditions contrôlées tout en cherchant à identifier l'effet de divers paramètres tels que: la taille des particules, la température, le pH des solutions, la concentration des particules dans la solution, la vitesse d'agitation, l'influence de l'utilisation d'eau recyclée.

Les données obtenues ont servi à construire un modèle d'adsorption, dont les prédictions sont utilisées dans la modélisation d'un procédé au complet par le logiciel Aspen. Ce procédé a ensuite été validé dans ses points clés par un ensemble de tests expérimentaux :

- Lixiviation des fluorures.
- Précipitation des fluorures des solutions contaminées par additions de calcium.
- Précipitation des sulfates par addition de baryum.

3.4.1 Mesure des concentrations des fluorures en solution.

La méthode utilisée afin de déterminer les concentrations de fluorures est la méthode du SPADNS. (Hatch DR/2010 Spectrophotomètre). C'est une méthode colorimétrique, qui consiste à faire réagir les fluors avec un colorant rouge à base de zircon. Le spectromètre est pré-calibré et lit la concentration en colorant et affiche directement la concentration en fluor mesurée. La réaction se traduit par une décoloration de la solution. Afin de vérifier la précision de telles expériences, l'utilisation d'étalon interne a été systématique. Ainsi, une solution de concentration connue en fluorure (0.99 ppm) a été systématiquement ajoutée aux solutions mesurées afin de vérifier la précision de la mesure. Trois solutions de contrôle étaient systématiquement mesurées (30%, 50% et 70% d'étalon). Si les résultats n'étaient pas cohérents la solution à mesurer était systématiquement éliminée. Au cours des essais, cela n'est arrivé qu'une dizaine de fois. Lors des premiers essais de lixiviation, les concentrations de fluorures mesurées ont été comparées à celles obtenues en procédant à un bilan de masse sur les résidus de brasques.

Ce type de test est extrêmement sensible à de toutes petites quantités de produits interférents. La verrerie utilisée, avant de faire les mesures a systématiquement été décontaminée dans de l'acide. Comme recommandé, toutes les expériences ont eu lieu en utilisant la même verrerie de façon à limiter les interférences.

Aussi de façon à vérifier l'effet de l'adsorption possible de fluor lors de la filtration des échantillons, la composition en fluor des solutions a été mesurée avant filtration et après filtration. Des différences non négligeables (10% de différence) sont apparues seulement lorsque la concentration était supérieure en 5 g/L en fluorure. Dans ce cas, seule la concentration issue des prélèvements avant filtration a été utilisée.

Les espèces responsables des interférences sont les suivantes :

Tableau 3.2: Espèces responsables d'interférences dans le cas des mesures de fluorures.

Substance	**Concentration**	**Erreur provoquée**
Alcalinité ($CaCO_3$)	5000 mg/L	-0.1 mg/L F-
Aluminium	0.1 mg/L	-0.1 mg/L F-
Chlorure	7000 mg/L	+0.1 mg/L F-
Ion ferrique	10 mg/L	-0.1 mg/L F-
Ortho phosphate	16 mg/L	+0.1 mg/L F-
Hexametaphosphate de sodium	1.0 mg/L	+0.1 mg/L F-
Sulfate	200 mg/L	+0.1 mg/L F-

Les interférences provenant de l'aluminium peuvent être détectées en lisant la concentration de fluor à 15 minutes d'intervalle. Une augmentation appréciable de la concentration suggère une interférence provenant de l'aluminium. Attendre deux heures avant de prendre la mesure permet d'éliminer jusqu'à 3.0 mg/L d'aluminium.

3.4.2 Mesure des concentrations de Sulfate.

La méthode utilisée afin de déterminer les concentrations de fluorures est la méthode de précipitation avec le baryum contenue dans l'additif SulfaVer4 Sulfate reagent (Hatch DR/2010 Spectrophotomètre). C'est une méthode de mesure basée sur la turbidité. Elle consiste à faire précipiter les sulfates avec du baryum afin de modifier la turbidité de la solution. Le spectrophotomètre est pré calibré lit la concentration selon la turbidité et affiche directement la concentration en sulfate mesurée. Afin de vérifier la précision de telles mesures, l'utilisation d'étalon interne a été systématique.

Ce type de test est peu sensible à des quantités de produits interférents.

Les espèces responsables des interférences sont les suivantes :

Tableau 3.3: Espèces responsables des interférences lors des mesures de sulfates.

Substance	**Concentration**
Calcium	20 000 mg/L
Chlorures	40 000 mg/L
Magnésium	10 000 mg/L
Silicium	500 mg/L

CHAPITRE IV :

MISE À JOUR DES PROCÉDÉS DE TRAITEMENT DES BRASQUES : CINÉTIQUE DE DESTRUCTION DES CYANURES À HAUTES TEMPÉRATURES.

4.1 Présentation de l'article.

Ce chapitre reprend l'article intitulé **'Update on Spent Potliners Treatments: Kinetics of Cyanides destruction at High Temperature'.** Cet article a été accepté pour publication à la revue I&ERC.

La revue de littérature présentée au chapitre précédent a souligné le très grand nombre de procédés développés. Cet article reprend cette revue tout en se consacrant à l'étude de la destruction des cyanures uniquement. Trois types de traitement existent :

- Lixiviation puis oxydation en milieu liquide.
- Destruction thermique par oxydation à hautes températures (500-850°C).
- Destruction thermique lors de la liquéfaction des brasques.

Du fait de leur efficacité, et de la souplesse du procédé pour le traitement des fluorures qui doit ensuite être mené, les procédés basés sur le traitement thermique à hautes températures ont été retenus comme la solution technologique la plus prometteuse en absence de facteurs locaux pouvant influencer les critères de décision. Cependant, ce type de procédé est confronté à un problème d'agglomération des particules à des températures supérieures à 800°C.

L'article souligne l'importance de l'obtention d'une cinétique de destruction des cyanures. C'est une cinétique particulièrement difficile à étudier, ce qui explique qu'aucune donnée n'existe dans la littérature à ce sujet. Afin d'obtenir ces données cinétiques, les brasques sont introduites dans un lit circulant fluidisé interne, et le temps de résidence des particules y est varié. La concentration de cyanures résiduels est ensuite mesurée à intervalles de temps réguliers afin d'en déduire une cinétique de réaction. La cinétique ainsi dérivée est testée en la comparant aux résultats de traitement thermiques décrits dans la littérature, afin de valider les prédictions du modèle. Le peu de données disponibles dans la littérature limite tous autres types de validation.

De plus, afin de contrer les difficultés d'opération liées à l'agglomération, plusieurs additifs sont ajoutés aux lits fluidisés et les effets de ces derniers sont mesurés. Un mécanisme d'action impliquant l'enrobage des particules de brasques par des particules d'additifs est ensuite décrit. Il en ressort que des particules inertes, de petites tailles constituent un bon additif, prévenant l'agglomération.

Cet article démontre qu'il est souhaitable que la destruction des cyanures se fasse de manière thermique, et fournisse une cinétique de réaction permettant de réaliser l'optimisation des niveaux de températures et de temps de résidence.

4.2 Update on Spent Potliners Treatments: Kinetics of Cyanides destruction at High Temperature.

Yann Courbariaux, Jamal Chaouki*, Christophe Guy. (2004) :
'Update on Spent Potliners Treatments: Kinetics of Cyanides destruction at High Temperature'. Submitted to *I&ECR.*
Keywords: Spent potliners, Thermal treatment, Circulating fluidised bed, Agglomeration, Kinetics, Cyanides, Aluminium.

4.2.1 Abstract

A review of the technologies available to treat the cyanide content of spent potliners is presented. The various strategies of treatment are compared. Processes involving the combustion of spent potliners at temperature close to 800°C were selected as the most cost effective approach. It was found that designers of such processes are confronted with the lack of data concerning the kinetics of cyanides destruction of spent potliners and the occurrence of agglomeration.

This paper addresses both issues by showing that small quantities of additives are necessary to smoothly operate combustion processes and by presenting a simple model to predict the amount of additive needed in well-mixed conditions. In addition, for the first time, the apparent kinetics of the destruction of cyanides in spent potliners at high temperature are presented.

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4.2.2 Introduction

Aluminium is found in nature only in an oxidized form and must be reduced before being processed. The reduction is carried out in cells of about 1 to 1.5 meters in height, 5 to 15 meters in length and 3 to 5 meters in width.

The production of aluminium involves alumina as the main source of aluminium. Carbon is the specie being oxidized and carbon dioxide is the main by-product.

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2 \qquad (1)$$

The reduced aluminum metal generated is on the bottom of the cell and is siphoned out on a continuous basis[1].

The cells are filled with a molten bath of cryolite (Na_3AlF_6) which can be generated in two different ways:

$$3NaF + AlF_3 \rightarrow Na_3AlF_6 \qquad (2a)$$

$$6NaOH + Al_2O_3 + 12HF \rightarrow 2Na_3AlF_6 + 9H_2O \qquad (2b)$$

Alumina is liquid at temperatures close to 2050°C. However operating the process at these temperatures would be too costly. Consequently the alumina fusion temperature is lowered by using a mixture of cryolite (80-85%) and alumina (2-8 %) forming an eutectic melting at 950°C[1,2]. The liquid bath in the reduction cell is submitted to a current between two electrodes, forcing the reaction (1) towards the formation of aluminum. The anode is composed of carbon and suspended above the molten bath. The lower tip of the anode is in contact with the molten bath. As the reaction proceeds, the carbon is consumed and the anode is slowly lowered into the bath to provide some new carbon for the reaction. The cathode is composed of steel bars protected by a carbon layer. It is not consumed during the reaction; nevertheless during its lifetime it undergoes a slow degradation. The content of the bath slowly infiltrates the cathodes and can crystallize leading to the formation of cracks. As well, secondary products can be generated by the reaction involving chemical species adsorbed onto the carbon layer. In addition, nitrogen from the air above the cell can react with the carbon of the electrode and the sodium content of the bath to form some cyanides salts such as NaCN.

$$2Na + 2C + N_2 \rightarrow 2NaCN \qquad (3)$$

After three to eight years, the cathode must be replaced. The discarded cathodes are then called 'Spent Potliners'. Spent potliners content is highly variable but usually contains aluminum in the 5-20% range as well as refractory bricks (20-50%), carbon (5%-50%), sodium (7-20%) and calcium (1-3%) etc. This waste is considered hazardous because it contains some highly toxic species such as cyanides (0.1-0.7 %), fluorides (20%) and PAHs in high concentration and in contact with water, cyanides can react in order to generate vapors of highly toxic hydrogen cyanide and a caustic solution containing dissolved cyanides. In the mean time, reactions occurring when contacted with water inside the spent potliners result in emissions of hydrogen and methane, which, in unventilated area can lead to explosions. Moreover, on a long-term basis, leaching of fluoride from spent potliners stored in landfill sites can translate into the contamination of rainwater runoffs if left uncontrolled.

After numerous studies and contradictory decisions, in September 28th 1998, the U.S. E.P.A ruled to forbid the landfill of spent potliners without adequate treatment. As a result, aluminum producers are faced with the problem of the disposal of huge amounts of spent potliners[3].

There are about a dozen aluminum producers in the US; Canada numbers 12 producers, 11 of which are in the province of Quebec. On an annual basis, it is estimated that about 800 000 to 1 millions tons of spent potliners are produced in the world. Quebec, alone, produces more than 50 000 tons of spent potliners a year. Over the years, most of it has been piling up in dedicated warehouses, and awaiting treatment. Treatment of spent potliners represents a huge financial burden for most aluminum producers. Pawlek, in 1993 evaluated the average cost of treatment for a ton of spent potliners at about $1000 U.S[4]. The huge financial potential gain has attracted lots of interest and several companies have been working on the development of processes to treat effectively spent potliners. Consequently, numerous potential treatment strategy studies have been published in the literature.

However, to this date, no processes have been found efficient enough to be accepted in the market as a universal standard. So far, many aluminum producers are working in their own backyard to develop its own process. Most of them consider recycling material to local markets as a viable option in order to improve the economics of the process. However that makes developed processes dependent upon the local conditions where it is located. As a result, there is no universal answer to this decade old problem. Consequently the need still exists to find a standard, efficient, flexible, and economical way to treat spent potliners.

This article will focus on the treatment of the cyanides contained in spent potliners. Fluoride treatment will be considered in a later article.

Numerous strategies have been developed to handle this waste with respect to the cyanide content.

Cyanides are thought to be the result of the reaction between nitrogen from the air, the carbon from the liners and the sodium content of the bath, leading to the formation of

NaCN salts. They are not distributed evenly in the spent potliners and are mainly found in the cooler region of the cell, near the surface in contact with air. When cyanides are stored outdoors, as time goes by, contact is made with water. Most cyanides will then react with water and any rust available to create a very stable iron cyanide complex $(Fe(CN)_6)^{4-}$. The unreacted cyanide salt is highly soluble and will be washed out by rain[5]. Consequently, 90% of the cyanides found in old spent potliners are ferrocyanides[4]. Ferrocyanides are much more difficult to oxidize than cyanides salts[6].

Three categories of treatment can be used to effectively treat cyanides. They can be basically classified according to the temperature of the process (see tables 4.1,4.2 and 4.3).

1) Low temperature processes: 25°C to a 100°C. (Leaching)

Cyanides are first leached by water and then treated separately using a wide range of technologies such as oxidation, UV treatment, zinc precipitation or others. Fluorides are partially leached along with the cyanides.

This type of treatment requires long residence time and harsh chemical conditions (NaOH or sulfuric acid) in order to leach significant amount of cyanides. Furthermore the destruction of cyanides in the solution obtained is difficult and often necessitates high temperatures, up to 250°C[24]. As well, fluorides are partially leached in this operation, which can complicate its treatment[18]. Investments cost will be high due to the large reactor volume made necessary by the long residence time. Operating costs will be high due to large volume of water that needs to be heated in order to reach the temperature necessary to oxidize the cyanides.

Table 4.1. Low Temperatures processes based on the leaching of cyanides and its subsequent treatment.

Process	Size of particles (mm)	Spent potliners treatment by steps (1., 2., 3.)	Residence time	Conditions	Initial composition of cyanides (mass/mass)	Efficiency of cyanides removal by steps.
Alcan[5,7,8,9]	<0.5	1. Three basic leaching. 2. Hydrolysis in high-pressure vessels.	1. N/A 2. 1 hour	1. 80-90 C. 2. 182 et 15 MPa in pressure.	N/A	1. 600 ppm in leached liquid. 2. 99.9 %
Rethmann[10]	<0.1	1. Three basic leaching 2. UV-oxidation	1. N/A 2. 2 to 4 hours	1. 80 C Likely to be ambient.	0.05 %	N/A
Blayden[6]	<10	1. Batch leaching in water. 2. Reacting cyanides with sodium hypochloride.	1. 2 hours	1. 25-80°C	0.15 % to 1.25 %	1. 95 % leaching. 2. 89 % oxidation
Bush[11]	0.1	1. Basic leaching 2. Acid leaching 3. Cyanides are volatilised and then incinerated.	N/A	N/A	0.067 %	N/A
Pong[12,13]	-	1. Water leaching 2. Precipitation with zinc 3. Oxidation of precipitate	N/A	N/A	2.5%	1. 98.8 %

Table 4.2. Mid temperatures processes based on the oxidation of spent potliners.

Process	Size of particles (mm)	Spent potliners treatment	Residence time	Conditions	Initial composition of cyanides (mass/mass)	Efficiency of cyanides destruction
Reynolds[14-16]	50	Oxidation in rotative drums.	90 minutes	540 to 760ºC	2.8 % 0.34 %	98.6 % 95.2 %
Comalco[17-20]	1	Oxidation in Torbed (fluidized bed) without carbon combustion.	N/A	550 to 700ºC	0.1 % to 0.7 %	71% to 81 %
Ogden[21, 22]	<50	Circulating Fluidised Bed oxidation	30 minutes	780 to 870ºC.	2 %	<99.99%
Divine[23]	1	Steam oxidation.	N/A	800ºC	N/A	N/A
Deutschman[24]	20	Small rotative drum.	48 minutes	350ºC	0.055 %	Low

Table 4.3. High Temperature processes based on the vitrification of the spent potliners and the imprisonment of cyanides in glassy material. N/A: Not available in the literature.

Process	Size of particles (mm)	Spent potliners treatment	Residence time	Conditions	Initial composition of cyanides (mass/mass)	Efficiency of cyanides destruction
Ormet[1,25]	0.4	Oxidation in Vortec reactor.	N/A	1200 to 1500° C	N/A	N/A
SPLIT[26,27]	2.5	Oxidation in a Vortex reactor	5 seconds	1100 to 1800°C Particles are heated at least to 750°C.	0.1 %	Leaching reduced by 96.8 %
Ausmelt[2] [8,29]	25.4	Oxidation in a molten slag bath	N/A	1300°C	N/A	N/A
Elkem[30]	15	Oxidation in a molten slag	N/A	N/A	N/A	N/A

2) Mid temperatures processes: from 500 to 850°C: (Combustion)

Cyanides are destroyed by oxidation while still on the particles of spent potliners. Residence times are much lower, but temperatures need to be maintained low in the combustion unit, in order to avoid agglomeration. In spite of efficient temperature control, it is often necessary to add special additive to the spent potliners in order to limit the risks of agglomeration. Fluoride are mainly unaffected by this process but could be fixed to some extent by the addition of limestone and formation of CaF_2. Investments costs are relatively low thanks to the short residence time and low corrosive characteristics of the combustion gases. Most of the heat will be provided by the combustion of the carbon fraction of the spent potliners, will result in lower operation costs.

3) High temperature process from 1100 to 1300°C: (Vitrification).

Cyanides are treated by oxidation while spent potliners are being vitrified. The remaining cyanides are not leachable. In order to vitrify the spent potliners, very high temperatures are reached. Fluorides are then vaporized and transformed into hydrofluoric acid (HF) by contacting them with steam. The high temperature and the corrosive nature of the combustion gases result in higher cost of operation for this type of processes. Furthermore, most vitrification processes rely on the massive addition of additives to produce glassy material that will be retaining fluorides in its structure once cooled down. These additions translate into increased energy costs induced by the heating of these extra materials to very high temperature[8].

Cyanide concentrations in spent potliners (0.1 to 0.5 %) as well as conditions of treatment vary from one process to another. The large variations in the raw material complicate the process optimization and cost minimization. In order to minimize costs, minimum residence time and optimum temperature for the treatment of cyanides should be known. However for the low and high temperature processes, cyanides destruction conditions optimization cannot be performed independently. Indeed, the fluoride treatment and its optimization will be strongly affected by any change to the conditions of treatment of cyanides. These processes will not be easily adaptable to any change in the composition of spent potliners. As a result they are designed to handle any type of wastes in the worst-case scenario.

Consequently type 1 and 3 operating and capital costs are considered to be higher compared to type 2 processes. In most cases, developers justify the extra costs by relying on the improved recycling opportunities for the mineral content of spent potliners. However, most industries are reluctant to recycle the content of the treated spent potliners. The use of former hazardous waste in their processes could be detrimental to their image and complicated from a legislative point of view[16].

In conclusion, it appears that the most promising treatment option is the combustion of spent potliners and a separate treatment of the fluoride content of spent potliners unless recycling options are available locally[31].

With the most promising technological option of treatment selected, mainly two problems remain to be tackled:

- What are the apparent kinetics of cyanide destruction?
- How to limit the agglomeration of spent potliners.

4.2.3 Issues under consideration.

The knowledge of the kinetics of destruction of cyanides at high temperatures is an essential tool for the design of optimised processes. A technology can truly efficiently treat any type of spent potliners residence only once residence time and temperatures have been effectively predicted. Furthermore, the EPA in its study on the evaluation of technologies to identify the BDAT (Best Demonstrated Available Technology) underlines the lack of data concerning this type of kinetics. In order to evaluate the efficiency and the global reach of a technology, it is of the uttermost importance that the kinetics of cyanides destruction be known.

Few detailed studies are available on the subject of cyanides thermal destruction:

Kasiderredy et al. [9] and Fortin et al. [32] have studied the kinetics of cyanides oxidation in a liquid at temperatures lower than 250°C. They found that cyanides oxidation kinetics is a first order reaction.

Balla et al.[33] to our knowledge published the only study related to the oxidation of cyanides at high temperatures from 292 K to 1500 K. However their studies deal only with CN radicals in the gas phase. They report finding a first order reaction too.

Deutschman et al.[24] report the results of their experiments which consisted of submitting spent potliners to a thermal treatment involving steam between 300-400°C in an autoclave. A few points are obtained and residence time of 60 minutes is necessary to reach 99.5% destruction of cyanides at 300°C and 99.8% at 400°C.

Agglomeration of spent potliners:

Spent potliners were found to agglomerate at low temperatures, in the vicinity of 800°C. Particles can stick to each other as the result of the melting of the surface of the particles of spent potliners. Tabury et al.[34] found that the 'glue' of the agglomeration was composed of 51% F, 30% Na, 16 % Al and traces of others compounds.

Agglomeration is a major problem for most high temperature reactors such as fluidised beds or rotary kilns. Once the agglomeration of particles starts, the distribution of particle size changes and the hydrodynamics are modified. As a result the larger particles lose their ability to exchange heat and their temperature increases, which leads to more agglomeration. The entire content of a reactor can agglomerate in a few minutes. In order to circumvent this problem, two strategies can be used.

The first one is based on temperature control:

- Temperatures can be kept too low for the agglomeration to take place (e.g. Comtor or Reynolds processes). This is made possible by limiting the combustion of the carbon content of the particles, which prevents the apparition of local hot spots. However this is not easily performed and agglomeration problems can still occur very likely due to the existence of local hot spots[16].

- Temperatures are kept so high that spent potliners are melted and cannot agglomerate in the reactor (Vitrification processes).

The second approach relies on the use of additives:

Additives are used to smooth out the operation of combustion units at high temperatures, but at the cost of handling larger quantities of material. For example the Reynolds process in a rotary kiln, involves the addition of 1 ton of sand per ton of spent potliners in order to prevent agglomeration. Tabury et al.[34] studied the agglomeration of spent potliners in a fluidised bed and concluded that 3 to 8 times the weight of spent potliners in additives are necessary to control agglomeration. Rickman[21,22] estimated to 20 % of the spent potliners initial weight, is the amount of additive needed for combustion in a circulating fluidised bed.

It is important economically to reduce to a minimum the amount of additives added to the reactor in order to:

- Limit the amounts of residues to be landfilled after the thermal treatment.
- Reduce the heat needed to run the process.
- Reduce the cost involved in the purchase of additives.

4.2.4 Experimental

Characterization of the type of spent potliners used during this study

Various tests have been carried out on the spent potliners in order to characterize them:

4.2.4.1 Elemental analysis of the spent potliners used for the experiments.

Table 4.4 summarizes the elemental composition of the spent potliners selected for the experiments. The composition of cyanides, carbon and fluorides are slightly lower than the value generally found in the literature, but not out of range. It is not expected that the higher than usual proportion of the inert compound (refractory) will affect the treatment of the hazardous fraction of the waste.

Table 4.4: Typical composition of spent potliners.

Composition of spent potliners used in this study.	
Carbon	<14 %
Fluorides	14%
Cyanides	0.038%
Aluminums	13 %

4.2.4.2 Thermogravimetry analysis.

The experiments were carried out using a pure oxygen atmosphere as the carrier gas.

Two phases were observed during the experiments:

- The first phase started at 90°C and ended in the vicinity of 230°C. This phase is traditionally labeled 'devolatilization phase'. It corresponds to the emission of volatile compounds, such as sulfur dioxide, methane and hydrogen.

- The second phase, corresponding to the combustion itself, is initiated at about 350 °C and ends at 800°C.

The devolatilization weight loss amounted to a little more than 1% of the weight of the sample, whereas, the combustion weight loss amounted to 14 % of the weight of the sample. Once again, this tends to indicate that the combustible content of the spent potliners is rather low.

4.2.4.3 Sieve analysis.

Crushing was used to reduce the average particle diameter of the biggest particles of the sample of spent potliners. The size distribution of the particles can be found in table 4.5. This table, as well, indicates the weight loss after combustion in an oven at 800° C. Sieving the particles will not allow the separation of refractory and carbon particles as there is little difference in weight loss (carbon faction) between small particles compared to bigger particles.

Table 4.5. Sieve analysis results and weight loss of each fraction after combustion.

Fractions	Sieves (µm)	Mass fraction (%)	Weight loss fraction (%)
1	>710	22.2	13.8
2	500-710	15.9	15.8
3	355-500	11.2	12.8
4	180-355	12	12.4
5	75-180	19.6	8.8
6	<75	19	10

4.2.4.5 Neutron activation analysis

Neutron activation analysis is an analytical technique which allows for the determination of the composition of various elements in a sample. Table 4.6 indicates the elemental concentration of aluminum, fluorine and sodium of spent potliners samples before and after combustion in an oven at low temperature (800°C). Combustion results in the removal of the carbon content of the sample and leads to the concentration of other chemical species such as fluorine and aluminum. The last rows of the table indicate the calculated concentration of these elements if the assumption is made that they remained completely in the sample and with the effect of weight loss due to the elimination of carbon removed. As can been concluded from these results, fluorine and sodium likely remained in the sample. However, the lower than expected percentage for the aluminum tends to indicate some aluminum or aluminum containing compounds vaporized during the combustion process.

Table 4.6. Measured and calculated of elements, after combustion.

Measured Percentage	Al (%)	F (%)	Na (%)
Untreated Spent potliners	13.4	12.8	14.7
Spent potliners heated at 800°C in an oven.	16.6	14.4	16.7
Calculated percentage if a 14% weight loss of carbon is taken into account.	15.5	14.8	17

4.2.5 Determination of the apparent kinetics of cyanides destruction.

The apparent kinetics of cyanides destruction are difficult to obtain for various reasons:

- Spent potliners are classified as hazardous wastes since fluoride (HF) and cyanides (HCN) emissions can occur at high temperatures. The stringent security measures taken in consequence, limit the extent of the experiments that can be performed. This is likely the main reason why no data can be found in the literature concerning cyanides combustion.

- High sample weights are required for cyanide analyses to be performed, a minimum of 10 g of sample is needed for each analysis of total cyanide content.
- Sample temperature should be uniform during pre combustion heat-up and during combustion, which can be difficult when high sample weights are used.
- Particles should be heated without being in contact with oxygen and without being submitted to high gas flow in order to reduce NaCN salt evaporation.
- Residence time of the particles during combustion should be well-controlled.
- Particles should be quenched immediately after undergoing partial combustion for analysis purposes.

Consequently, the Internal Circulating Fluidized Bed (ICFB) was selected to carry out the experiments. The ICFB has been described in details elsewhere[35]. The reactor schematic is presented in figure 4.1. Basically, it is composed of two columns introduced one into the other. The central one is the riser (height 1.23 m, diameter 8 cm), where the solids travel upward pneumatically, propelled forward by a mixture of hot air and combustion gases originating from the natural gas burner located below the riser. The velocity of the air through the riser can reach 10 m/s. Top to bottom temperatures in the riser are very homogenous because of solids circulation, leading to a less than 5K gradient. Temperatures reported in this study represent the temperature averaged over the length of the riser. The external cylinder, (height 2.3 m, diameter 30 cm) contains a downward moving bed of particles and is called the annulus. The particles circulate from the external cylinder to the internal cylinder through 8 holes drilled at the bottom of the riser.

The external cylinder is used to preheat the particles to temperatures varying from 500 to 700°C depending on the application, whereas the internal cylinder is used for treatment of the particles, by contacting them with hot air coming from the burner.

Residence time in the riser and annulus can be controlled by varying the air velocity inside the riser and the injection of secondary air at the bottom of the annulus.

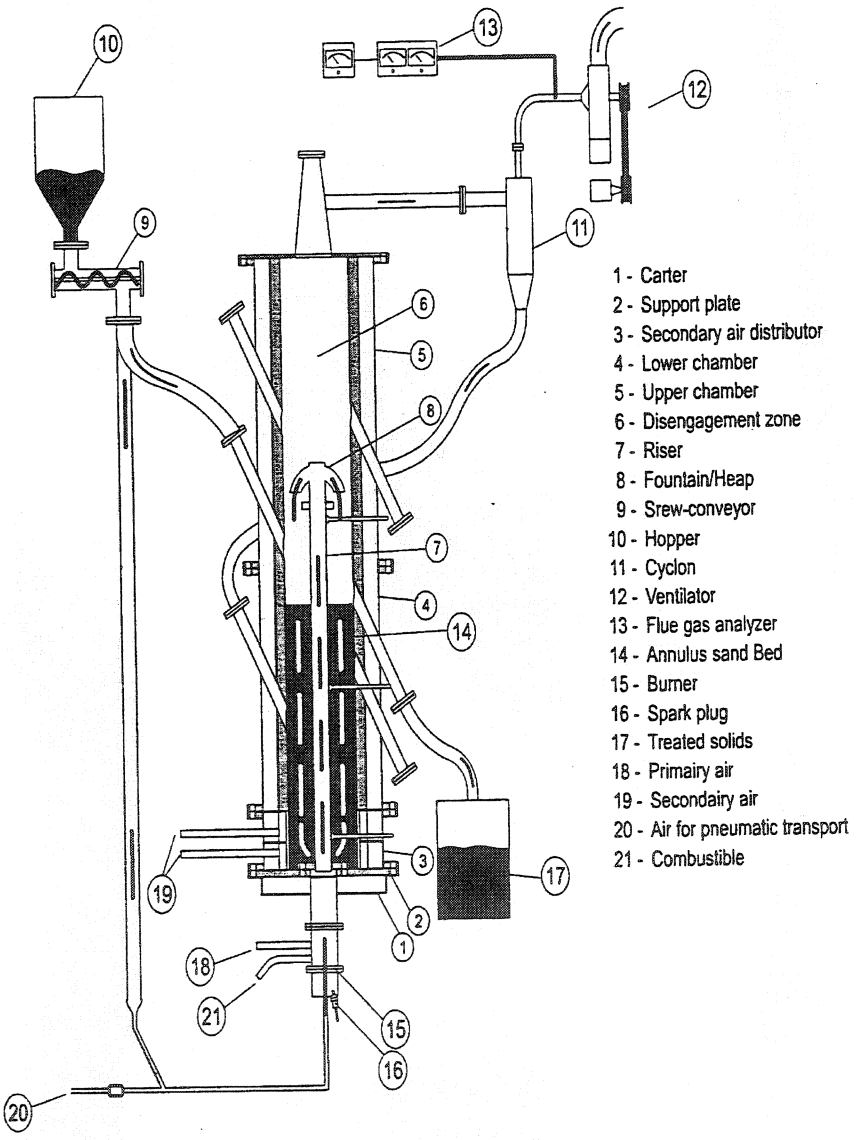
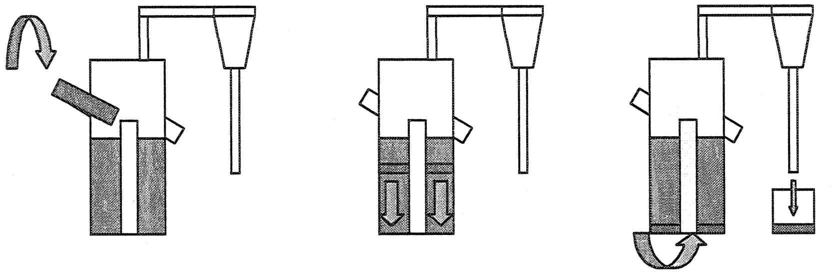
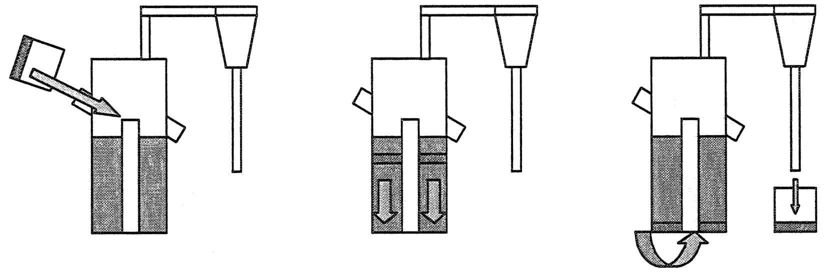


Figure 4.1: Schematic of the internal circulating fluidized bed (ICFB).

During an experiment, the reactor is filled with spent potliners (147 kg). The natural gas burner is used to heat the particles in the reactor and to control the oxygen content in the riser. The oxygen concentration in the riser varied during the course of the experiment between 5% and 7%. No secondary air is injected to the annulus and its oxygen content is zero. After steady-state is reached, feeding of fresh spent potliners is stopped. A batch of up to 500 g of very fine spent potliners particles is introduced in the annulus, over a period of about 1 minute to reduce the effect of the injection of cold material in the bed. The small particles mix with the hot particles coming from the riser and are then heated in the annulus for 7 minutes. The annulus temperature varied from 500 to 620°C top to bottom. After reaching the bottom of the annulus, they then pass only once in the riser before being collected at the exit of the cyclone. The fine particles of spent potliners are separated from the rest of the particles at the fountain and quenched in the freeboard to a temperature of less than 450°C, thanks to a significant air flow at room temperature introduced in the freeboard by the opening of the screwfeeder. Upon exiting the reactor, the temperature drops to 230°C. A sample of particles is collected after each cycle and sent for total cyanide content analysis in an external lab whereas the rest of the particles are reinjected into the reactor for further treatment. This way, it is possible to control the residence time of the small size particle sample. The number of 'feeding-collecting' cycles in the bed is used to determine the total residence time in the riser for these small particles. Figure 4.2 illustrates this process. The drawback of this method lies in the fact that for each cycle, part of the sample is lost since not all the particles of the sample are retained by the cyclone. For an initial weight of 500 g, the maximum number of cycle that can be performed is about 20.



Injection of spent potliners Spent potliner Circulation Fine collection



Fine reinjection Fine circulation Fine collection

Figure 4.2: Description of the steps used in the experiments carried out to determine minimum residence time for the destruction of cyanides.

The residence time in the riser is evaluated by using the validated ICFB hydrodynamic model developed by Mukadi et al.[36] and based on the resolution of the following momentum equation:

$$V_p \frac{dV_p}{dz} = g \frac{\rho_g - \rho_{SPL}}{\rho_{SPL}} \left[\left(\frac{U_o / \varepsilon - V_p}{U_o / \varepsilon_\infty - V_{p_\infty}} \right)^{1.4} - 1 \right] \qquad (1)$$

Where V_p represents the particle velocity, z the height in the riser and g the gravity acceleration. U_0 represents the gas velocity in the riser and is obtained by using the ideal gas law knowing the flow rate of natural gas and air fed to the burner (see table 4.7). ε and ε_∞, represent the voidage along the entire length of the riser and in the fully developed zone, respectively. ε is obtained through mass balance consideration (mass of solid/volume of gas) whereas ε_∞ is deduced from Patience et al.[37] correlations in the fully developed zone of a circulating fluidized bed.

Table 4.7. Properties used in Mukadi's model[38].

Properties.	Value	Properties.	Value
Volume of annulus	0.11 m^3	Air flow to the burner	29.23 m^3/h
Total weight of spent potliners	147 kg	Natural gas flow	1.85 m^3/h
Solid circulation rate	73.5 $kg/(m^2.s)$	Bulk density of spent potliners	1350 kg/m^3.
Voidage	97.6 %	Particle density	2120 kg/m^3
Emissivity of particles	0.90*	Quenching air flow	60 m^3/h
Cp of particles	0.82* kJ/(kg.C)		

*estimated.

The ICFB configuration was selected for this kinetics evaluation because it presents many advantages for this type of study:

- It is designed to handle high sample weight continuously in constant operating conditions.
- After staying in the annulus, the spent potliners are all heated at the same high temperature before entering the combustion zone. At steady-state, the 500 g sample of the spent potliners particles at room temperature is mixing with hot particles from the riser. The resulting mixture is estimated to reach thermal equilibrium in less than 1 second using Mukadi et al.'s model[36] and neglecting convection heating.
- If the same model is used to evaluated heating time in the riser, equilibrium temperature is reached in less than 0.01 seconds even when only radiative heat

transfer is considered. This is due to the large surface area of the small particle size used.

- In the annulus, particles are heated with no gas circulation. Consequently evaporation of sodium cyanides is negligible when equilibrium of NaCN vapor pressure is considered[38]. The high volume of spent potliners treated ensures that possible oxygen infiltrations have a negligible effect.
- Temperature and oxygen content in the riser are almost constant due to the low concentration of particles and short residence time which does not allow significant carbon combustion to take place. Residence time is easily controlled by varying the temperature and gas flow rate in the riser. Residence time in the oxidative zone of the reactor was calculated using the model developed by Mukadi et al.[36].
- Particles upon exciting the riser are separated in two fractions, the high size particles fall back onto the moving bed, whereas, the small size particles studied are entrained in the freeboard. Radiation cooling from walls, low solid concentration and low gas temperature due to the massive introduction of room temperature air explains why quenching is almost immediate. A radiative heat transfer model derived from Mukadi et al.'s work[36] has been used to estimate the cyanides conversion in the freeboard in a hypothetical worst case scenario. Convection cooling was neglected and it was assumed that the departing particles of the freeboard are submitted on half of their surface to the temperature of the hot particles in the riser (800°C) and the other half to the radiation coming from the wall. When this model is combined with the cyanides destruction kinetics, conversion in the freeboard was shown to amount to less than 0.25% for each cycle.

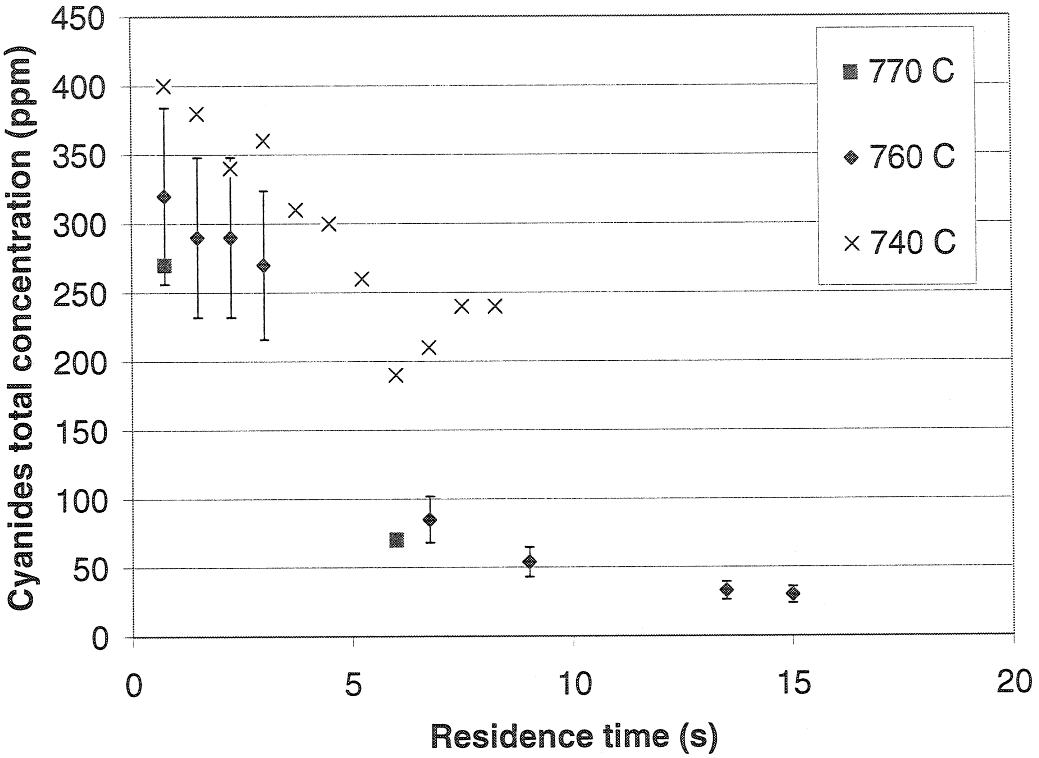


Figure 4.3: Concentrations of cyanides with respect to the residence time in the oxidative zone of the ICFB.

Three tests were run and the results are presented on figure 4.3. Few data points were obtained because each analysis reduces the sample size and limits the number of cycle that can be performed. The data were then assumed to reflect the order found in the literature for low temperature experiment, and so a first order reaction was considered.

Consequently expression (2a) and (2b) were used to model the results obtained.

$$\ln\frac{C}{C_o} = -kt \qquad (2a)$$

$$\ln k = -\frac{E.A}{RT} + \ln(k_0) \qquad (2b)$$

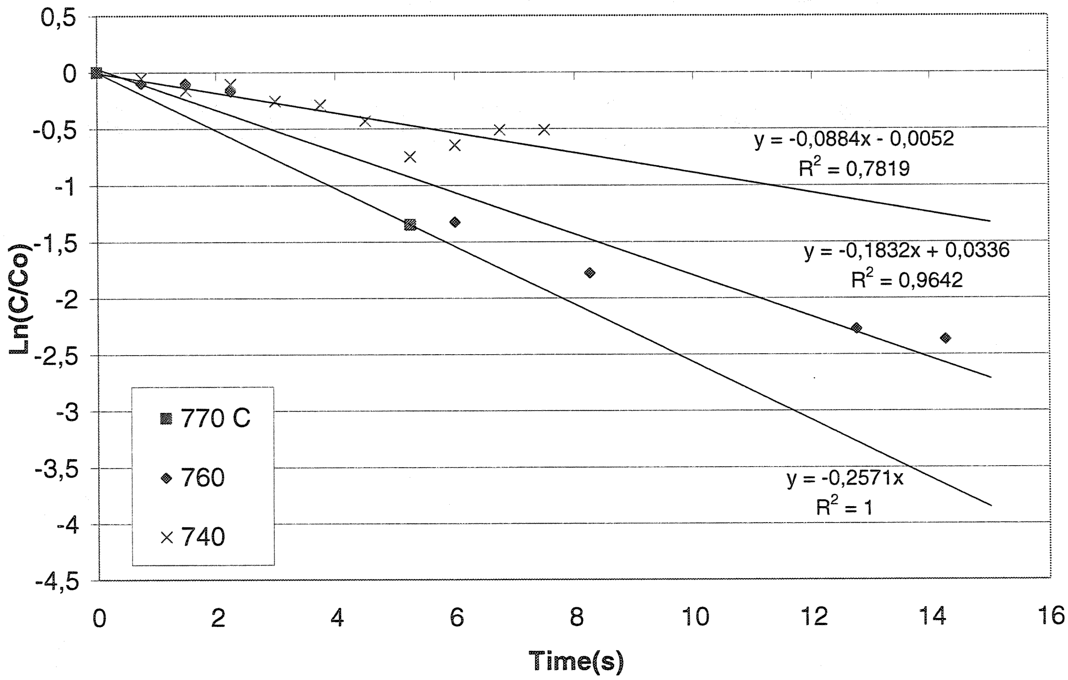


Figure 4.4: Determination of the kinetics parameters for a first order reaction.

Figure 4.4 represents ln(C/C_o) plotted with respect to time. A linear relationship is found. If the slopes obtained are then plotted with respect to the inverse of temperature, the activation energy (E) can be found (cf. figure 4.5)

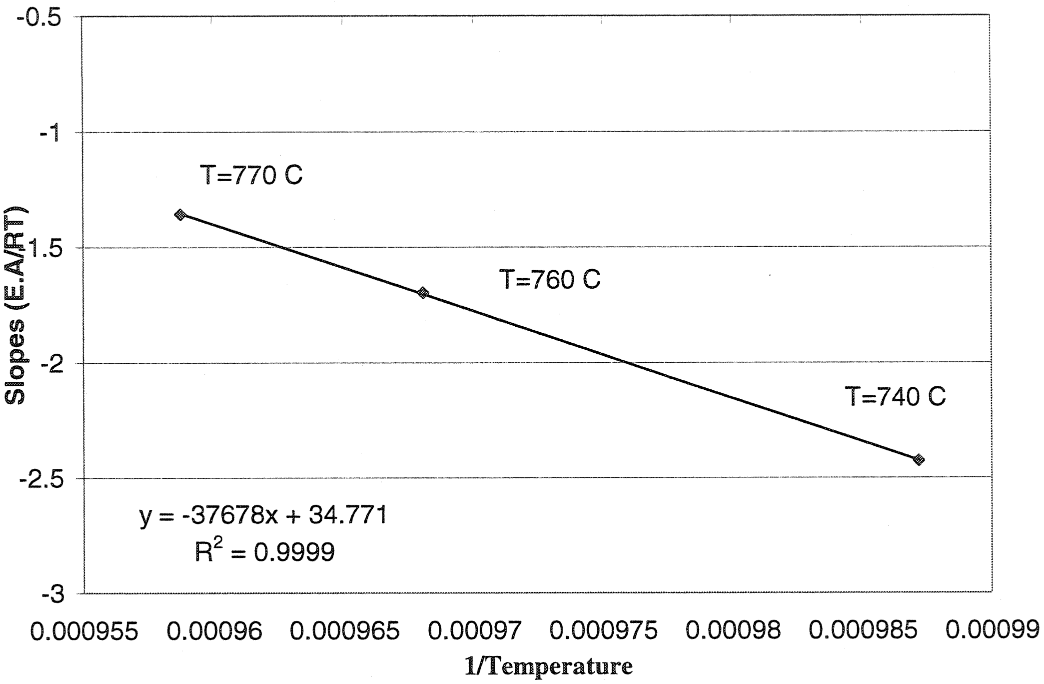


Figure 4.5: Determination of the Activation Energy of spent potliners destruction.

Consequently, it was found the rate of destruction of cyanides was best represented by setting the activation energy (E) at 312 (± 8%) kJ/mol and the preexponential factor k_0 at $1.26*10^{15}$ (± 65%) s^{-1}. Errors percentage reported were estimated by the perturbation method, assuming error on cyanide measurements to be 20%, 30 K for temperature readings, and 5% error on residence time evaluation and assuming independent error for both activation energy and preexponential factor.

In order to validate this expression, predictions were made and compared with the scant data available in the open literature. Table 4.8 lists the various parameters characterizing some processes found in the literature and compares the results reported with calculated predictions.

Table 4.8. Comparison of predictions to industrially reported results.

Process	Reported Average conversion	Reported Residence time (Second)	Reported temperature (Celsius)	**Calculated temperature to reach conversion**
Reynolds	97 %	5400	560-760	620°C
SPLIT	96.8 %	5	>750	795°C
				Calculated Residence time to reach conversion
OGDEN	> 99.99 %	1800	760-870	<47 seconds
				Calculated conversion at the indicated temperature
Deutschman	'Not satisfying'	2800	350	$5*10^{-4}$%

In spite of the lack of data, the kinetics are in agreement with the results obtained in the literature. Consequently, optimisation could be performed on some processes listed in table 4.8. In particular, the residence time in the Ogden process can be considerably lowered and the temperature in the Deutschman process should be increased.

4.2.6 Anti-Agglomeration additives study.

Spent potliners used in this study where found to agglomerate at temperatures in the vicinity of 800°C. This result is similar to values found in the literature[21]. In operation, spent potliners agglomerate mainly at the bottom of the annulus, when particles caught in the moving bed contact the hot surface of the riser. Agglomeration does not take place in the riser likely because of low solid holdup conditions (low probability of collision between melting particles in the riser). However, if an obstacle is introduced into the riser, such as a plate or a rod, then the solids concentration rises in the vicinity of the obstacle and limited agglomeration can occur locally.

Table 4.9. Properties of the four additives used in this study.

Name of the additives	Properties
Additive a)	Small particle size (10 μm). Basic properties and contains alkaline species.
Additive b)	Sand with average particle diameter of 220 μm.
Additive c)	Very small particle diameter (2.5 μm), inert material.
Additive d)	High particle size (750 μm), weak basic properties, combustible.

Four additives have been used in order to limit spent potliners agglomeration. Their properties are described in table 4.9. Due to proprietary reasons the exact nature of the additive cannot be disclosed. The performance of these additives at increasing the temperature of agglomeration has been tested in an oven, and the results are summarized in table 4.10.

Additive a) had a dismal performance at increasing the temperature of agglomeration. It had to be expected, because alkaline species have been showed to decrease the melting temperature of some type of ashes[39]. If used in the ICFB, agglomeration occurs immediately.

Additive b) (sand) was not tested in an oven but only in the ICFB. With a mixture containing a maximum of 30 % SPL, a minimum of 70 % sand, the ICFB could reliably be operated without observing any agglomeration.

Additive c) and shredded additive d) presented similar performances in the oven, but full size additive d) was ineffective in the ICFB. Agglomeration occurred in every runs even at additive d) concentrations higher than 50 %. However, a mixture of 25 %

additive c) and 75% spent potliners has been successfully used to run ICFB tests. The reactor could be operated for more than 30 hours without encountering operational problems.

Table 4.10. Agglomeration temperature of mixtures of additives and spent potliners in an oven. Additive b) performance was not tested.

Composition of the mixture tested	Nature of additives	Agglomeration Temperature in oven	Behaviour in pilot unit
25% additive 75% SPL	a)	< 760°C	Immediate agglomeration
50% additive 50% SPL	a)	< 760°C	
75% additive 25% SPL	a)	< 760°C	
20% additive 80% SPL	c)	860°C	No agglomeration in bed even with additive concentration lower than 10%
25% additive 75% SPL	c)	> 900°C	
30% additive 70% SPL	c)	850°C	
50% additive 50% SPL	c)	< 760°C	
75% additive 25% SPL	c)	< 760°C	
25% additive 75% SPL	Shredded d)	850°C	Unsuccessful with non-shredded particles.
50% additive 50% SPL	Shredded d)	860°C	
75% additive 25% SPL	Shredded d)	> 900°C	
Additive b)	b)	N/A	Agglomeration when additive proportions lower than 50%.

In spite of its efficiency, the main handicap of additive c) lies with the small particle size of of the additive. An important proportion of the additive was entrained in the riser and was not retained by the cyclone. If this additive was to be used industrially, the need would arise to better separate particles and gas, as well as to recirculate the additive particles. In addition, as a proportion of the additive is not retained in the reactor, it implies that the minimal proportion of additive c) in the mixture could be lowered below 25% and still be effective.

In order to calculate the lower the amount of additives needed, an understanding of the anti-agglomeration mechanism of action is necessary. The exact nature of the additive action is not known, but they are thought to present two possible mechanisms of action to prevent agglomeration[40]:

1. Modification of the eutectic composition of the melted layer of particles[41,42].

2. Dilution of the spent potliners in order to make agglomerated material still manageable by weakening the agglomerated material bonding[39].

One mechanism of action does not exclude the other. These mechanisms necessitate large amount of additives in order to have a significant impact and effectively reduce agglomeration risks. It is likely that the Reynolds process and Tabury et al.[34] had to resort to these methods in order to limit agglomeration impact in their studies.

However, it can be noted that additive c) and shredded additive d) were predicted as having similar anti-agglomeration properties in the oven test when used with small particles size. Nevertheless, only small size additive c) had an impact during the ICFB run. It is likely that particle size is a factor that cannot be neglected, even though it is not mentioned in most anti-agglomeration studies.

Tangsathitkulchai et al.[40] and Linjewile et al.[43] in their investigation of coal ashes agglomeration and additive mechanism stress the fact that for agglomeration to occur, particles must first come into contact with each other. The same remark can be made about additives: to be effective, they must first come into contact with SPL particles. Ideally the additives should cover entirely the surface of all spent potliners particles. Observations of the bed inventory after the experiments showed that anti-additive particles coated the SPL particles and did not seem to have reacted with them since they remained detachable. The particles of SPL covered with anti-additive particles can no longer contact each other. Consequently, when submitted to temperatures higher than their agglomeration temperatures for short periods of time, they will not be able to agglomerate.

By geometrical considerations, it then possible to predict the minimum amount of additive needed to cover bigger particles. (See figure 4.6).

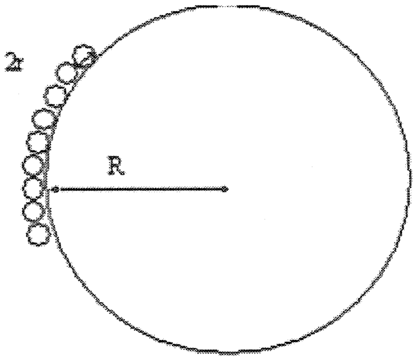


Figure 4.6: Geometrical considerations in the case of coating of the particles by additive.

If the fluidised bed inventory is composed only of particles of radius R_0, then the total surface of one spent potliners particle is defined as:

$$S = 4\pi R_0^{\ 2} \tag{3}$$

The surface occupied by a single particle of additive of diameter r, onto the surface of the SPL particle is:

$$s = \pi r^2 \tag{4}$$

Consequently, the minimum number of particles of additives needed to cover the entire surface of one single particle of spent potliners can be calculated:

$$n = \frac{S}{s} = \frac{4{R_0}^2}{r^2} \qquad (5)$$

With the assumption of perfectly spherical particles.

As a result, the minimum fraction P of additive that must be added to the spent potliners to prevent agglomeration is:

$$P = \frac{n * \frac{4}{3}\pi r^3 \rho_a}{\frac{4}{3}\pi R^3 \rho_{SPL}} = \frac{4r}{R_0} * \left(\frac{\rho_a}{\rho_{SPL}}\right) \qquad (6)$$

Often, the density of the additive and the spent potliners are similar. Therefore when considering our distribution of particles, the minimum percentage of additives particles needed should have been of the order of 6.5-8 % which is significantly lower than the quantities reported by Tabury[34] and for the Reynolds process.

To validate these calculations, a test was carried out where the proportion of additives was lowered to 10 %. No agglomeration occurred. However, spent potliners and the additive had to be well mixed before being introduced in the reactor (see figure 4.7). Even though the entrainment rate was greatly lower in this experiment compared to the previous one with 25% additive, entrainment still occurred. Consequently, the real percentage of additives in the bed must have been even lower than 10 % due to the higher removal rate of the additives compared to spent potliners.

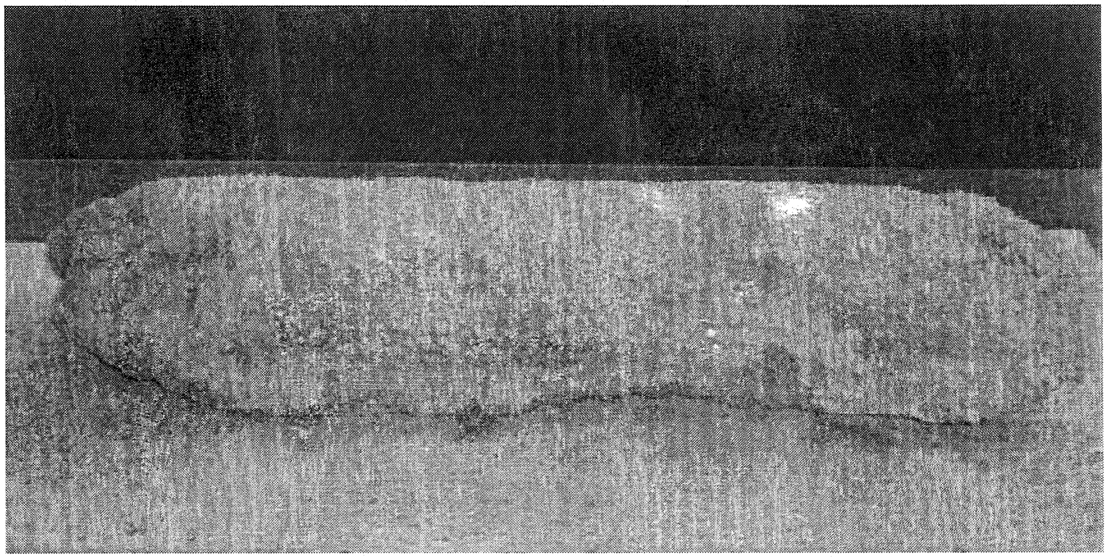


Figure 4.7: 40 cm-long pieces of agglomerates (ICFB). The white stain on top of the sample is the anti-agglomeration additive which is not incorporated in samples of spent potliners.

The coating mechanism described to explain anti-additive properties will only be valid:

- In reactors, where particles agglomerate when traveling in hot spots for short period of times, which is the case of the ICFB. To operate a fluidized reactor at temperatures beyond melting point of particles requires chemical modifications of the melting layer of particles along with higher concentrations of additives[44].
- Very small particles size of the additives.

For big particles to be coated with additives, forces must exist to hold them together. Numerous studies are reported in the literature of inter particles forces balance and agglomeration mechanisms[45,46]. Agglomerate existence is due to five types of forces[47] (Van der Waals, Liquid bridges, Sintering, Electrostatic and Chemical forces). Since in this study, the additive particles sticking to the particles are easily detachable, it can be assumed that Van der Waals forces could be the driving force leading to the coating of particles. If this is the case, good coating of SPL particles without modifications of the particles can be obtained only with very small size additive particles (1 or 2 microns) in order to present significant Van der Waals forces. Bigger particles will not stick to non-melting particles. This is likely why sand and additive d) with their large particle size did not present good anti-agglomeration properties in the pilot unit bed when used in small proportions.

4.2.7 Conclusion:

Spent potliners cyanides destruction studies have been reviewed. It was found that the most sensible way of designing a universally applicable low-cost process to the treatment of spent potliners was to separate the cyanides from fluorides treatment through the use of medium temperature oxidation technologies. However the optimisation of the design of thermal treatment unit requires the knowledge of the kinetics of cyanides destruction, as well as the use of anti-agglomeration additives. The experimental study carried out on a pilot unit of an internal circulating fluidised bed allowed for the operation of a spent potliner combustion unit by using only a proportion of only 10% additives. A simple model has been developed to predict the minimum proportion of additives that needs to be used in well-mixed reactor depending on particle size. Arguably, the best way to lower the industrial quantity of additives needed for the process is to improve the mixing characteristics of the reactor used and to reduce the size of the additive particles.

As well, the destruction kinetics of cyanides in spent potliners were found to be a first order reaction presenting an activation energy (E) of 312 (± 8%) kJ/mol and a preexponential factor k_0 of $1.26*10^{15}$ (± 65%) s^{-1}.

The scant results available in the literature were successfully compared to the proposed kinetics predictions. Improvement to this apparent kinetics law could be obtained by evaluating the effect of particle size in order to obtain the real kinetic laws.

4.2.8 Acknowledgment

This research was funded in part by Cintec Inc. and Polysolutions inc.

Nomenclature

C : Cyanides concentration (ppm).

C_0 : Initial cyanides concentration. (ppm).

E : Activation energy (kJ/mol).

g: Gravity acceleration, 9.81 m/s^2.

k_0 : Prexponential factor (s^{-1}).

n : Number of particles of additives needed to cover on SPL particle.

P : Proportion of additive needed with respect to the weight of SPL.

r : Additive particle radius (m).

R_0: Spent potliners particles radius (m).

R: Universal gas constant.

s : Surface spent potliners particle occupied by additive (m^2).

S : Surface of one spent potliners particle (m^2).

T : Temperature (K).

U_0 : gaz velocity in riser (m/s).

V_p : Particle velocity in riser (m/s).

V_{p_∞} : Particle velocity in the fully developed zone of the riser (m/s).

z : Height in riser (m).

ε : Average voidage in riser.

ε_∞ : Voidage in the fully developed zone of the riser.

ρ_g : Gaz density (kg/m^3).

ρ_{SPL} : Spent potliners particle density (kg/m^3).

ρ_a : Additive particle density (kg/m^3).

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CHAPITRE VI :

DÉTERMINATION DE LA CINÉTIQUE DE COMBUSTION ET DE DÉVOLATILISATION DES BRASQUES PAR THERMOGRAVIMÉTRIE.

5.1 Présentation de l'article

Le chapitre précédent a montré que l'incinération était la meilleure option de destruction des cyanures et que des additifs peuvent être utilisés afin de contrôler l'agglomération. Cependant, la température du réacteur doit être contrôlée de façon étroite afin de faire en sorte que celle-ci reste en dessous des 800°C. Cela peut poser de grandes difficultés étant donné que les brasques contiennent une forte proportion de carbone, qui est facilement combustible. Ce chapitre fournit une cinétique de combustion et de dévolatilisation des brasques, qui permettra de contrôler la combustion des brasques, et permet de démontrer que dans le temps nécessaire à la destruction des cyanures, la combustion du carbone des brasques a juste débutée. Ce chapitre est constitué d'un article intitulé **'Modeling of spent potliners devolatilisation and combustion by thermogravimetry analysis'** et a été soumis à la revue Fuel pour publication.

Les cinétiques ont été obtenues à l'aide d'une balance thermogravimétrique, en définissant préalablement les conditions de réaction nécessaires afin d'éviter les effets liés aux transferts de chaleur et de masse. Un processus très strict de fitting de mécanisme de réactions, impliquant les mêmes paramètres quelle que soit la rampe de chaleur utilisée, a été employé avec succès.

Le résultat de ce travail est un mécanisme cinétique très robuste et complet qui permet de prédire le déroulement des réactions de dévolatilisation et de combustion avec une précision très importante. A noter qu'un nouveau type de réaction contrôlé par la température plutôt que le temps de résidence, a été identifié, et que ce type de réaction a été modélisé par un mécanisme de réaction impliquant des énergies d'activation distribuées.

5.2 Modeling of Spent Potliners Devolatilisation and Combustion by Thermogravimetry Analysis.

Référence: Yann Courbariaux, Ramin Radmanesh, Jamal Chaouki*, Christophe Guy. (2004) : 'Modeling of Spent Potliners Devolatilisation and Combustion by Thermogravimetry Analysis'. Submitted to Fuel.

Keywords: Spent potliners, Thermal treatment, Thermogravimetry, Kinetics, DAEM model, linear weight loss, Heat and mass transfer.

5.2.1 Abstract:

Spent potliners are a by product of the aluminium industry. It is considered a waste throughout the world because of its cyanides and fluoride content. Thermal treatments technologies can be used to destroy the 0.6 % cyanides it contains. However, the high carbon content (10-69%) of spent potliners makes it a possible valuable resource as a energy source. In order to enable recycling, it is necessary to limit the combustion of carbon during thermal treatment. Consequently a good model of the pyrolysis and combustion behaviour of spent potliners is needed. In this paper, TGA experiments have been used to obtain an apparent kinetics pyrolysis and combustion mechanisms of the carbon content of the spent potliners, free of heat and mass transfer limitations. Four weight loss sections have been modeled: Drying, devolatilisation, coking and combustion. A Distributed Activation Energy Model with a flat distribution has been used to model the coking reaction, whereas the others reactions are modeled using the classical single reaction approach. The model obtained is very robust and relies on constant kinetics parameters throughout the experimental range. The predictions are on average within 0.24% of the experimental results.

5.2.2 Introduction

Aluminum production is based on the reduction of bauxite (Al_2O_3), taking place in electrolysis cells, called pots, with dimensions ranging from 1 to 1.5 meters in height, 5 to 15 meters in length and 3 to 5 meters in width (Chanania et Eby, 2002)

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2 \qquad (1)$$

The process involves the dissolution of bauxite in a cryolite bath in proportions of 18.5% to 81.5% respectively. The resulting mixture melts at 950°C which is a lower fusion temperature than bauxite alone, translating into energy cost reduction. Depending on the specificity of the process, other compounds in smaller proportion are added to the bath to facilitate the reaction (Silveira et al., 2002).

The exterior walls of the pots are made of a thick refractory layer designed to prevent heat losses. The refractory is lined up with carbon in which steel bars are embedded.

The steel bars are used to conduct the electricity necessary for the reduction reaction to take place to the bath. Since the content of the bath is extremely corrosive, steel bars cannot be put directly into contact with the bath. Thus, they are embedded in a cathode which will be manufactured in order to present the following characteristics (Grojtheim and Welch, 1988):

- Electrical conductivity as high as possible.
- Good physical contact with the steel bars.
- Closed pore structure in order to limit the contamination of the cathode with the content of the bath.
- Hard enough to withstand abrasion from the electrolyte.
- Low coefficient of expansion in order to limit cracking related to mechanical stresses.

Carbon type cathodes were found to be the best material meeting all of these requirements presented above. It can be manufactured by various methods: [Grojtheim and Welch, (1988), Silveira et al., (2002), Balgord, (1978), Brooks et al., (1991), Bontron et al., (1993)]:

- Preformed cathode blocks which are then bonded by a pitch-carbon paste rammed between joints.
- Preformed cathodes blocks which are carefully machined and then glued together.
- Ramming a plastic mixture of the pitch and calcined anthracite (or semi-graphite) with the insulated steel cathode shell to form a single monolithic block.

The preassembled cathodes are then heated to high temperatures in order to carbonize the pitch and harden the cathode. In this process the coal pitch turns liquid and can fill efficiently the pores of the cathodes which results in a good contact between the preembedded steel bars and the cathode blocks. (Wilkening, 1983).

In spite of its resistance characteristics, during the 5 to 8 years life span of cathodes, cryolite infiltrates its structure, and at the same time, cyanides and HAPs are formed in the carbonaceous structure. Progressively the cathode dissolves into the bath and the steel bars can be corroded. Upon failure of the cathode, often detected by the presence of iron in the bath, the liner is removed along with the refractory used to thermally insulate the cell. The resulting product is called 'spent potliners'.

The composition of spent potliners is variable, but on average contains 7-20 % Fluoride, 10-69 % carbon, 0.02-0.7 % cyanides, 3-23 % Aluminum and 0-49 % refractory (See table 5.1).

Spent potliners are considered a waste throughout the world. Although, national legislation varies, most target its cyanides and fluorides content for reduction objective before allowing definitive landfill. An extensive review of technologies available can be found in Courbariaux et al, (2004) and Pawlek (1997). This article will focus only on technologies requiring thermal treatment.

Table 5.1: Composition of spent potliners according to reference.

Spent potliners Composition.	**Brooks et al. 1992**		**Bontron, 1992**	**Reynolds 1996**	**EPA 1996**	**Brown and Reddy 1994**	**Pawlek, 1993**	**Kidd,1993**	**Ogden 1984 Reynolds**	**Ogden 1984 Alcan**
Aluminum	20.4	20.4	3-8	5-22	4-6	11.0	7-22	7.9-22.8	5	14
Refractory										
Carbon	24.8	16.9	25-55	10-50	50	25.0	13-69	9.6-57.5	43	29
Sodium	19.5	19.4	12-19	7-20	10-18	15.5	9-22	8.8-14.2	20	14
Cyanides			0.1	0.02 - 0.44	0.5	0.15	0.002-0.6	0.1-0.7	0.14	0.1
Fluoride	17.9	21.3	6-10	6-19	10-15	16.8	7-22	13.5-15.0	18	18
PAHs			-	-	<0.1				-	-
Phenols			-	-	<0.1				-	-
Silicium	0.79	0.03	<15			4.53	1-11	8.5-2.0	0.1	5
Calcium	2.26	2.0	1-2	1-3	1-3	2.54	1-2.6	1.9-1.3		
Iron	0.69	0.54	0-2	0-2	0-1		0.3-0.8	0.8-0.4		

There are two types of thermal treatment technologies currently being developed:

1) Mid temperatures processes (500 to 800°C).
2) High temperature processes (1100 to 1300°C).

Type 1) processes (Reynolds, Comalco, Ogden, Deutschman, Courbariaux) involves rotary drums (Reynolds, Deutschman); or fluidized bed (Comalco, Ogden, Courbariaux) and either the partial or total combustion of carbon (Reynolds, Ogden, Courbariaux) or limited combustion (Comalco, Deutschman).

Type 2) processes (Ormet, Ausmelt, Split, Elkem) involves batch vitrification in furnaces (Ausmelt, Elken) or circulating fluidized bed (Ormet, Split). Complete combustion is required for the Ormet and Ausmelt technologies, whereas, Elkem process gasifies the carbon and Split process leaves most of the carbon unburned. See article Courbariaux et al. (2004) for more detailed descriptions.

The carbon content of spent potliners is considered to be a valuable resource, because of its energy content (Divine, 1997) that can be used as a source of energy for the thermal treatment itself, or be recycled in other processes [Byers et al. (1986), Givens et al. (1989)]. As well, some researchers suggest that spent potliners carbon particles could be recycled in the fabrication of new cathodes. Depending on temperatures level, presence of oxygen, and residence time, the carbon content of spent potliners during thermal treatment could be reduced to zero or left untouched. Consequently, the fate of carbon is a key issue in the design of thermal treatments of spent potliners. No studies have been reported in the open literature involving the kinetics of spent potliners pyrolysis or combustion.

Thermogravimety constitutes an excellent tool to determine the apparent lumped kinetics of spent potliners pyrolysis and combustion. A detailed description of thermogravimety measurements principles can be found in reference (Haines P.J., 1995):

If x represents the conversion and is defined as such:

$$x=\frac{W-W_{initial}}{W_{final}-W_{initial}} \qquad (1)$$

It is then possible to define the reaction rate:

$$\frac{dx}{dt}=\frac{-dW}{dt}\bullet\frac{1}{W_{final}-W_{initial}} \qquad (2)$$

It is usual to represent the effect of temperature and conversion on reaction rate by the expression (3), which allows to evaluate separately the effect of temperature and conversion: (Conesa et al.,2001).

$$\frac{dx}{dt}=\mathrm{k(T)}^{*}\ \mathrm{f(x)}. \qquad (3)$$

Where k(T) is defined by the Arrhenius law:

$$\mathrm{k(T)}=k_0\bullet\exp(-\frac{E}{RT}) \qquad (4)$$

The function f(x) can adopt various expressions which will be found in the literature (Haines, 1995). The most common expression, but not the only one, is $f(x) = x^n$ where n designates the order of the reaction.

In order to identify the best expression describing the reaction rate with respect to the conversion, two types of approach exist:

1) Plotting a function involving the reaction rate measured and evaluated by expression (2) and an expression related to the assumed mechanism of reaction. The kinetics parameters are then changed till a straight line is obtained. The quality of the fit is then measured by the correlation coefficient. (Lee and Beck, 1984).

   For instance in the 'derivative' method, the logarithm of the reaction rate is used:

   $$\ln[(\frac{dx}{dT})/(f(x))] = \ln A - \frac{E}{RT} \qquad (5)$$

   Where A is equal to (k_0/β), and β represents the heating rate of non-isothermal experiments.

   The various possible expressions for f(x) (Haines, 1995) are varied in order to obtain the highest correlation coefficient. Time reduced plots (Avramov, 1985) and Integral methods (Brown, 1988) are two methods often used as well.

2) A direct search method which is not very often used in the literature due to the high computing time required. The optimal expression is found by varying the various parameters in order to minimize an objective function representing the quality of the fit. [Günes and Günes, (2002); Smieszek et al., (1982); Gabor et Antal, (1989), Gabor et Szabo, (2002)];. This approach requires the use of

mathematical software and usually does not resort to expression (2) to evaluate the reaction rates but is based on expression (6):

$$\frac{dW}{dt} = k(T)^{*} (W_{unreacted})^{n}. \qquad (6)$$

Approach 1) is certainly simpler and requires fewer efforts. However it suffers from various shortcomings. The most important difficulty lies in the manipulation of data due to the usage of logarithms and it is reinforced by the difficulty of defining when one reaction starts or finishes if two reactions overlap (Wilburn, 2000). Furthermore, the pyrolysis studies using this method necessitates the knowledge of the unreacted solid content of the particles for the apparent kinetics parameters of expression (2) to be related to the true parameters used in expression (6). However in pyrolysis studies, the mass of the sample, measured throughout the experiment represents the mass of unreacted solid, plus the char formed during the reaction. Therefore the conversion is not directly related to the unreacted weight of the sample and f(x) should be modified in consequence. (Conesa et al., 2001)

In this study, approach 2) was used to obtain the kinetics parameters corresponding to the model developed. The main advantage of this approach lies in the fact that the entire reaction can be fitted at once. The weight loss does not need to be separated in various sections related to various assumed reactions path and conversion does not need to be precalculated using expression (2). Thus, the final weight of the sample at the end of the reaction does not need to be assumed. Only expression (6) is used directly, which reduces the manipulation of data.

The main drawback of this approach lies into the high number of parameters that needs to be evaluated at the same time and the fact that the optimum found can be mathematically sound, but physically irrelevant (Salvador et al, 2003). In order to address the concerns concerning the validity of the parameters obtained, the approach was twofold:

From a physical point of view, the values of the parameters found were compared to other parameters found in the literature in order to check their relevance.

From a mathematical point of view, it is possible that various sets of initial parameters could yield an optimum fit: depending on the initial values selected, the simplex could converge towards different sets of parameters. To alleviate this difficulty, all the reactions were first roughly analyzed using the derivative methods described by Haines (1995) for all heating rates. This analysis yielded a range for each kinetic parameters that was used as initial guesses in the search algorithm. This range was the only one possible, since when very different initial values guesses converged towards different set of parameters they were not realistic (order of reaction found of 20 for instance) and obviously biased.

A second mathematical difficulty lies in the strong interactions of k_0, E and n [Himmelblau et al. (1970)]. However it is possible to visually, partially reduce the interactions of the parameters to improve fitting. The Activation Energy is strongly related to the temperature at which the reaction starts. Pre exponential factor k_0 defines how fast the reaction is going to be and how long it is going to take. The order of reaction is affecting the end of the reaction: a smooth end of the reaction indicates a low order reaction, whereas a high order reaction leads to a sharp end to the weight loss. These visual clues were used to help find the best initial values for the simplex algorithm. Finally, the fact that 7 different heating rates were used to fit the results sharply decrease the uncertainties in the fitting process, since there were always more experiments than parameters fitted in the reactions involved in a particular temperature range.

As a consequence of all the precautions taken in the fitting process, the parameters found are the unique ones describing correctly the experimental results and having physical relevance.

The differential equations describing the reaction were written and solved in Matlab using the stiff numerical solver ODE15S based on backward differentiation formulas. A Nelder-Mead simplex was used to find the optimum parameters with the minimized objective function being:

$$\alpha = \sum_{i=1}^{K} \sum_{j=1}^{N_i} \frac{\left| W_{predicted} - W_{measured} \right|}{N_i} \tag{7}$$

Where K represents the number of experiments performed at different heating rates and N_i is the total number of points. The experimental weight measurements were obtained at the rate of one point per second for each experiment. In order to obtain meaningful parameters, the number of experiments on which the parameters where fitted, where always higher than the number of parameters. In the case of this study, the number of experiments (K) is equal to 7, and the number of points fitted, depending on the experiments varied from 9299 points to a low of 665, for a total number of points fitted of 20559. Optimization was carried out for all experiments at the same time using all the points in order to give an equal weight to all the stages of the reaction. The objective function was chosen so as to directly represent the error committed between predictions and measurements (Smieszk et al., 1982).

When difficulties arise in fitting the experimental results, other approaches can be resorted to:

- The prexponential factor k_0 is considered not constant in the Arrhenius law but can vary depending on the temperature or the extent of the reaction. (Sharma et al., 1998, Arnold et al., 1982).
- The activation energy E is not a constant but is represented by a distribution. (Distributed Activation Energy Model or DAEM). (Caballero et al., 1995, Maki et al, 1997, Please et al., 2002, Liu et al. 2001).

However a mechanism of reaction is normally defined by a single set of activation energy and preexponential factor for any heating rates (Salvador et al., 2003). In spite of all the efforts invested in the precise determination of kinetics parameters, it is common that in models found in the literature, activation energy and preexponential factor measured will be changing depending on the conditions of experimentation. In order to explain why these supposedly constant parameters vary, numerous explanations have been proposed:

- Change of mechanisms in the sample and/or existence of a compensation factor [Chornet et Roy, (1980); Agrawal, (1985); Marban et Cuesta (2001)].
- Chemical reactions controlled by heat and mass transfer phenomenon. [Ollera et al., (2002). Antal et Varhegyi, (1997)].
- Inadequate representation of the mechanism of reactions. (Wilburn, 1999).

Using these artifices leads to very good predictions of TGA obtained results. However, when using the models based on these data, it is important to remember that most reactions studied with a TGA, are industrially carried out in fluidized beds for instance. These reactors are characterized by very high mass and heat transfer capabilities. If the kinetics obtained are only valid at low heating rates for instance, they will not be relevant for industrial applications or when the heating rate is changed. Furthermore, if the model developed relies on variable kinetics constants that need to be extrapolated from the TGA experiments obtained with constant heating rate, extrapolation will be very difficult in industrial conditions, where the heating rate is changing with time and the location of the particles (Salvador et al., 2003)

Consequently, thermogravimetry experiments should focus on obtaining apparent kinetics mechanisms and parameters that are very robust and free of the physical limitations related to the device used to perform the measurements (Ollera et al., 2002, Gabor et Antal, 1989). It is possible to obtain good quality reaction mechanism with a TGA only if the model can be used to predict the conversion at many different heating rates with the same mechanisms and the same kinetics parameters. (Salvador et al, 2003).

By applying this principle, Conesa et al, (2001) have shown that it was possible to identify a correct mechanism of Polyethylene degradation by varying the heating rate.

Once an adequate mechanism is obtained, extrapolation becomes more realiable. The 'true lumped kinetics' found this way can then be used in models taking into heat and mass transfer phenomenon to adequately predict conversions in industrial conditions (Di Blasi, 1996,1997).

5.2.3 Objectives of this study:

This study will focus on the determination of spent potliners pyrolysis and combustion kinetics free of heat and mass transfer limitations, and on the definition of a reaction mechanism capable of predicting conversion at various heating rates with constant kinetics parameters (Salvador et al., 2003).

Spent potliners compositions used for this study were obtained from Alcan, already crushed to a diameter less than 1 mm. Spent potliners used were sieved and 4 classes of particles diameter were selected: 45-75, 75-90, 90-125, and 125-250 microns. Apart from crushing and sieving, spent potliners used did not undergo any other treatments and retained their full content of cyanides and fluorides. A Mettler Toledo Thermogravimetry balance using 70 μL crucibles was selected to perform the experiments. Various temperature programs were prepared for the experiments to be performed. They all had in common:

- A 15 minute time period at 25°C in order to degas the sample, remove the oxygen content of the furnace (checked with a mass spectrometer) and stabilize the weight of the sample in an argon atmosphere.
- A 20 to 30 minutes time period at 800°C at the end of each experiment, in order to ensure that the reactions studied were finished and a stable final weight was obtained.
- An Argon atmosphere, fed to the furnace at the rate of 60 ml/min. When combustion was studied, oxygen was either fed with Argon right from the start of the experiment at a variable flow rate ranging from 20 to 80 ml/min, or only injected at 800°C at a flow rate of 20 ml/min. The argon atmosphere was used because using a nitrogen atmosphere would have interfered with the measurements of carbon monoxide concentrations using the mass spectrometer hooked up to the TGA.
- Various heat ramps were used: 5,10,20,30,40,50 and 70°C per minute, a factor 14 exists between the highest heating rate and the slowest one.

5.2.4 Heat and Mass transfer limitations:

The first objective of the study was to identify the conditions at which heat and mass transfer limitations are negligible in pyrolysing or combustion conditions. The three parameters studied were:

- Particle size (intraparticles mass transfer).

- Sample size (interparticles mass transfer).
- Temperature difference between set sample temperature and actual sample temperature. (heat transfer).

Since very small sample sizes are used in TGA experiments, ranging from 1 to 60 mg at most, consequently one small sample of particles is potentially not representative of the type of particles it is supposed to represent. The easiest indicator that can be used to characterize this issue is the ash content of the sample. On average, spent potliners used for this study contain 69 % ashes. However, the ash content found in a sample presenting a weight lower than 3 mg ranged from 87% to as low as 47 % ashes. For samples having an initial weight higher than 3 mg, the ash content varied from 64 % up to 75 % ash content. Consequently, low sample size minimizes heat and mass transfer limitations, but increases the problems related to the sample representativity. To tackle this issue, most of the results presented in this study and related to small size samples (less than 4 mg) actually represents the average of multiple experiments obtained with weight less than 3 mg and in the same conditions, till the sum of all sample size reached at least 10 mg. It is then expected that the experimental results will be representative of samples presenting an ash content of 69% ± 1.75 % [95%].

5.2.4.1 Particle size:

The effect of particle size was thoroughly investigated at heating rates of 5, 20, 30 and 50°C/min. It is expected that using particles with a large diameter will lead to intraparticular diffusion limitations of heat and gases. Figures 5.1 and 3.2 illustrates the results obtained at 20°C and 30°C/min for three different particle sizes and in combustion and pyrolysing conditions.

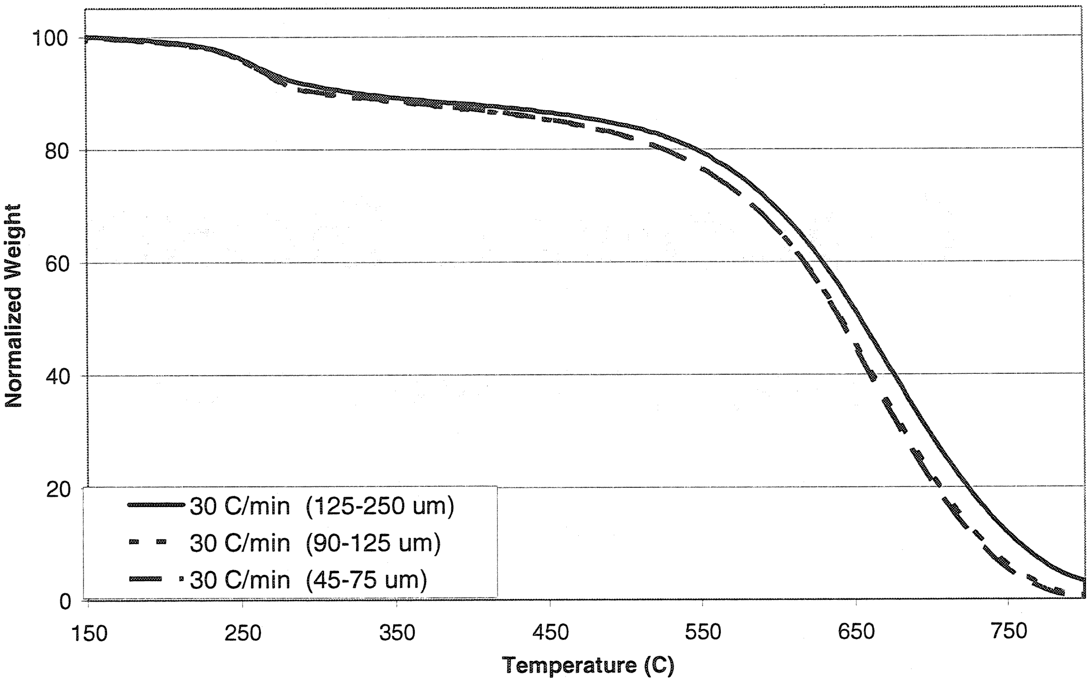


Figure 5.1: Combustion conversion with respect to temperature at a heat ramp of 30°C/min and three particle size (argon + oxygen atmosphere).

The results plotted represent the normalized weight loss which represent the true weight loss obtained divided by the weight loss obtained when the combustion is complete. The results, illustrated in the 20 and 30°C/min case, show clearly that very little difference is observed between particles presenting a diameter ranging from 45 to 125 microns. However 125-250 microns diameter particles present a slight difference compared to other particle size. Consequently, only particles with diameter lower than 125 microns were used in the rest of this study.

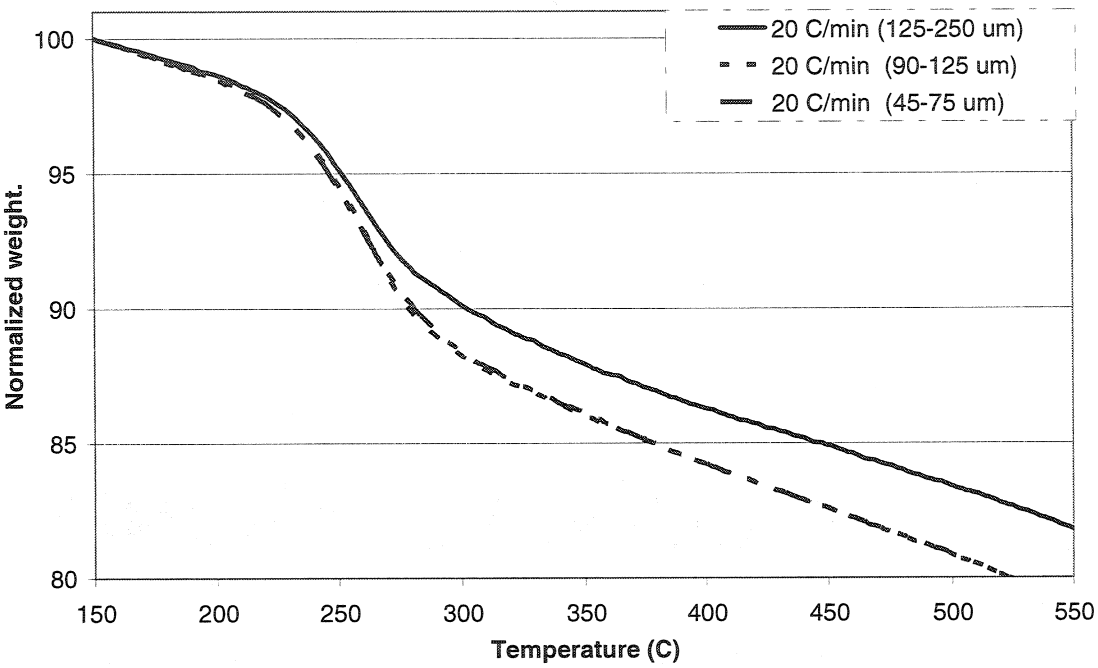


Figure 5.2: Pyrolysis conversion with respect to temperature at a heat ramp of 20°C/min and three particle sizes (Argon Atmosphere).

Sample size:

The effect of sample size was studied at 20°C/min in the case of pyrolysis. Experiments were carried for particles in the 45-75 um diameter range with various initial sample weight. 60 mg corresponds to a full crucible, whereas, mass lower than 4 mg corresponds to a one layer of particles at the bottom of the crucible. As illustrated by figure 5.3 and confirmed by other experiments at higher heating rate, the sample size has very little effect on the pyrolysis of spent potliners. Consequently, it is expected that in the range of experimentation, interparticular mass transfer limitations do not affect the pyrolysis reaction.

On the contrary, when combustion is studied, sample size has a very important effect, delaying the reaction, very likely because of mass transfer problem related to the diffusion of oxygen through the sample. In order to minimize the effect of initial particle weight, a series of experiments was performed involving 45-75 μm particles, heated to 800°C in an only argon atmosphere and then a mixture of oxygen plus argon was introduced in the furnace. Figure 5.4 illustrates the results obtained. With samples presenting an initial weight lower than 5 mg (mono-layer of particles on the bottom of the crucible), no difference in the rate of combustion can be noted. However, with bigger sample size an important difference appears.

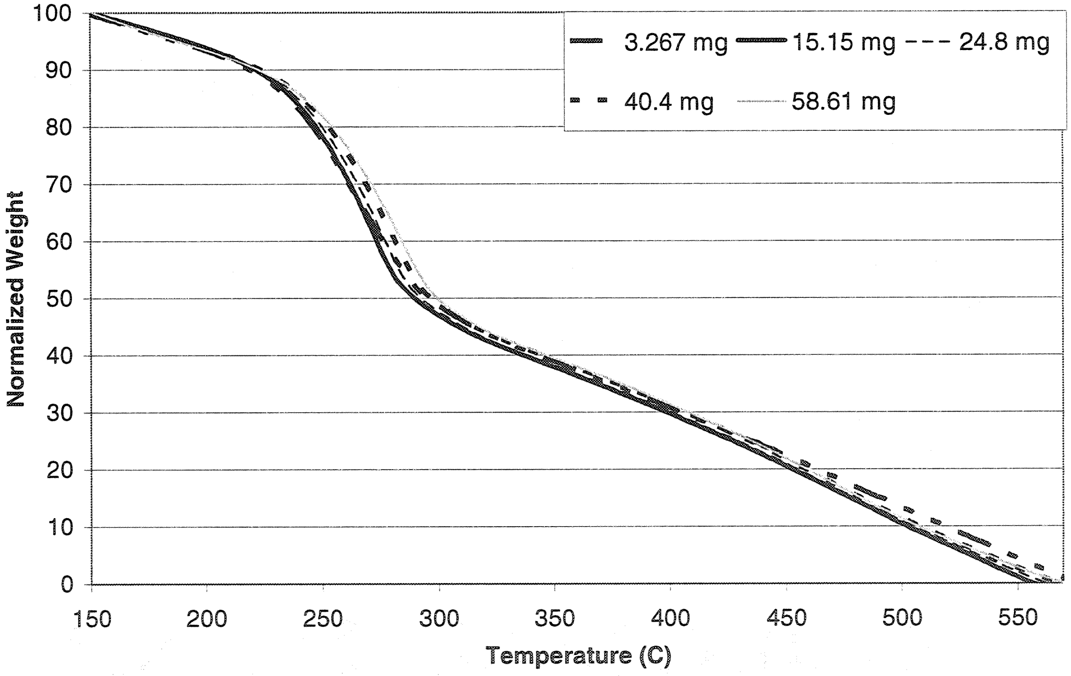


Figure 5.3: Pyrolysis conversion with respect to temperature at a heat ramp of 20°C/min and five sample size ranging from full crucible to crucible filled with one particle layer (argon atmosphere).

Consequently, both combustion and pyrolysis experiments were carried out with low initial sample weight and only mono-layer samples were used.

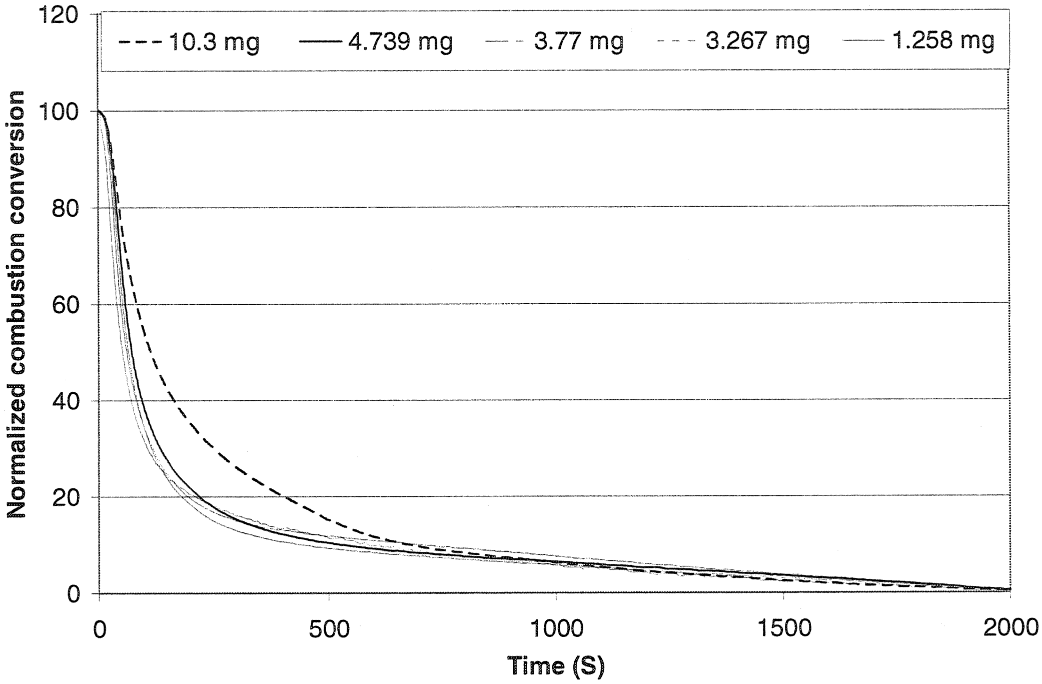


Figure 5.4: Combustion conversion at 800°C with respect to time for six sample size. Samples were heated to 800°C in an argon atmosphere, and oxygen was then added to the argon flow.

5.2.4.2 Heating rate:

Heat transfer limitations were evaluated by comparing the set temperature of the sample imposed by the thermogravimetry method compared to the temperature read by the thermocouple located under the crucible. This temperature does not represent exactly the sample temperature but is the best indicator of what the temperature would be in the sample (Conesa et al. 2001). The heat transfer limitations are characterized by a proposed parameter called the 'time lag'. It consists in measuring the difference of temperature between sample and set temperature in seconds representing the time difference between the moment the temperature is reached by the sample and the moment at which the temperature read should have been reached. The fastest thermogravimetry experiments takes between 11 minutes at heating rates of 70°C/minute to up to 155 minutes at 5°C/min.

Figure 5.5 illustrates the results obtained for samples of 45-75 µm particles and an initial weight less than 5 mg with combustion taking place. The highest time lag observed is 11 seconds for the 5°C/minute sample. Considering that the total experiment lasts about 155 minutes, this can be considered negligible. High time lag is observed too with the 70°C/min experiment. The lowest time lag corresponds to experiments with heating rate between 30 and 50°C/min. This good performance is likely related to the fact that heat is generated by the sample at almost the same rate that it should be generated by the furnace to reach the temperature set by the program.

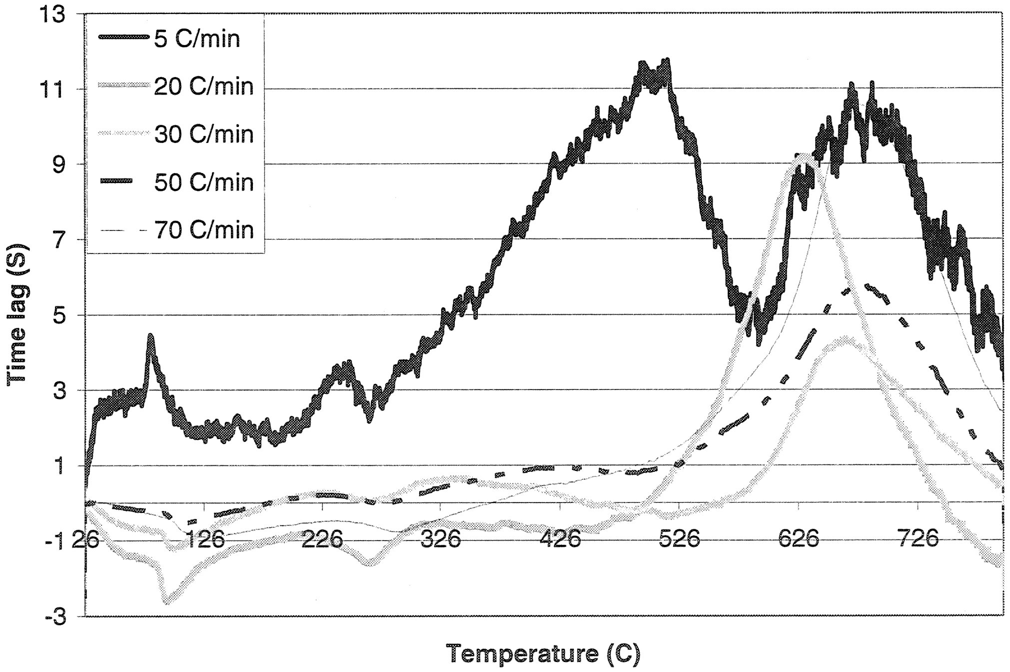


Figure 5.5: Time lag with respect to the temperature targeted for combustion of 4 mg sample 45-75 um in size for sample weight of 5 mg. (argon + oxygen atmosphere).

Consequently, it has been considered that the heat transfer is not a limiting factor in the experiments studied, even though it has the most important effect for experiments carried out at 5 and 70° C/minute.

5.2.5 Results:

Figure 5.6 presents the combined results of experiments carried out at heating rate ranging from 5°C/min up to 70°C/min. To identify the curves corresponding to a particular heating rate, keep in mind that the final weight increases along with the value of the heating rate.

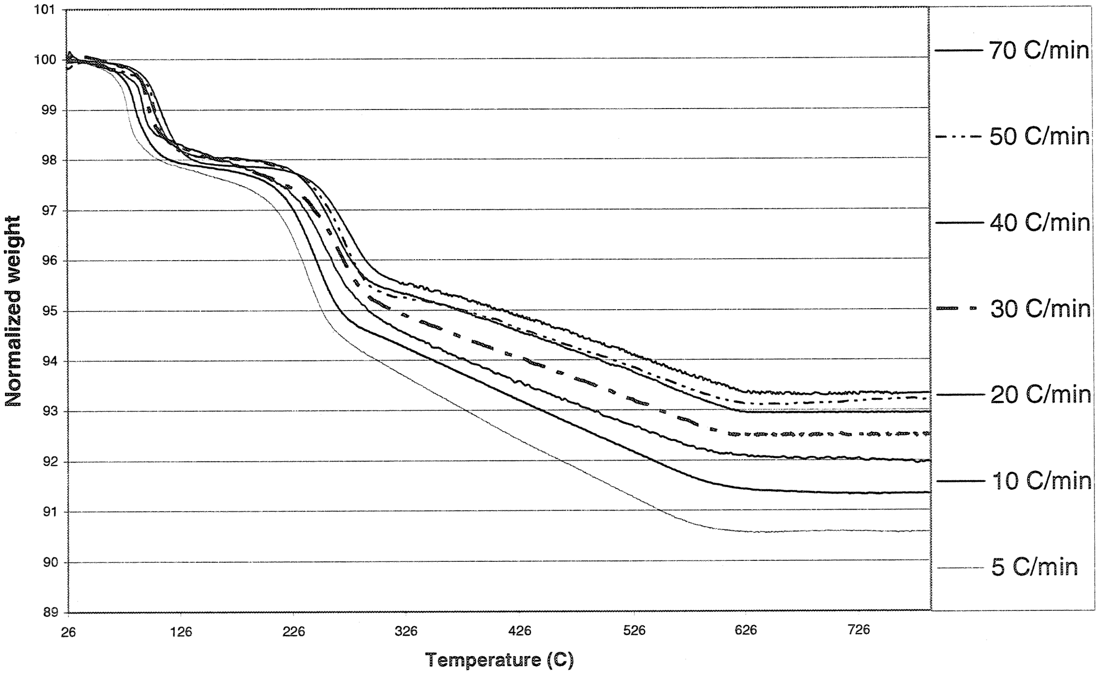


Figure 5.6: Weight loss versus temperature at different heating rates in absence of oxygen (argon atmosphere).

Three different weight losses section can be observed:

- From 50 to 150°C, a variable weight loss is observed limited to about 2.1% of the total weight of the sample. The mass spectrometer measurements allowed its attribution to water evaporation.
- From 150 to 320°C, a second phase of weight loss takes place amounting to about 3.5% of the total weight of the sample. Strong emissions of CH_4 and H_2 were measured during that phase by the mass spectrometer. It corresponds to the devolatilisation of spent potliners.
- From 320 to 630°C, a weight loss phase amounting to about 4 % of the total weight of the sample takes place. It corresponds to a second phase of devolatilisation, since, once again, high emissions of CH_4 and H_2 were measured.

Overall, devolatilisation corresponds to a 7.5% weight loss of the initial weight of the sample. It is surprising to realize that spent potliners, having been submitted to calcinations when manufactured and then to very high temperatures for a few years during their utilization as cathodes, can still devolatilize after being heated to 800°C. A few observations may explain these results:

- During their stay in the electrochemical cells, spent potliners undergo a series of reactions leading to the formation of HAPs. These are susceptible to devolatilize.
- During the dismantling of the cells, the still hot cathodes are watered abundantly to speed up cooling, actively promoting reactions between the water and the hot carbon compounds.
- Most spent potliners are stored outdoors awaiting treatment and in contact with atmospheric water which could lead to the formation of hydrogenated carbon compounds.

- Grinded spent potliners are more susceptible to undergo pyrolysing reactions at one atmosphere compared to the high pressure high density environment, they were submitted to previously.

Combustion studies were carried out in an atmosphere of mixed oxygen and argon. Figure 5.7 presents the combined results of experiments carried out at heating rate ranging from 5°C/min up to 70°C/min.

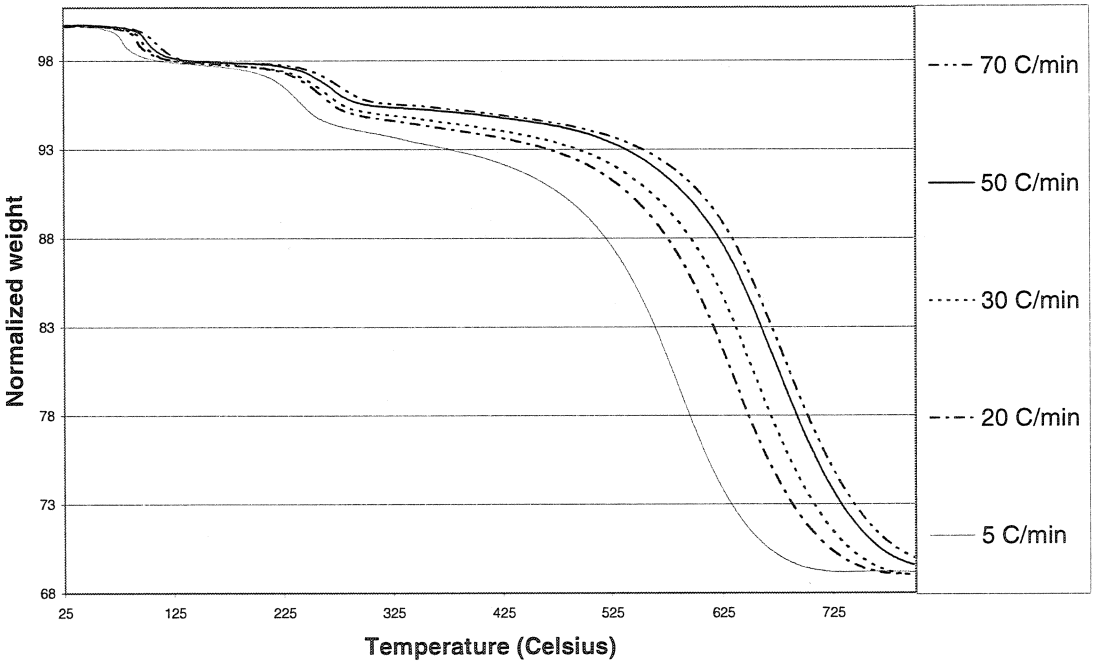


Figure 5.7: Weight loss versus temperature at different heating rates in the presence of oxygen

The three different weight losses zones observed in pyrolysis tests are similar to the ones observed in the combustion tests even though the weight loss due to the coking reaction (second devolatilisation) is not complete, since combustion starts off in the vicinity of 450°C before the second devolatilization finishes. Most of the reaction is finished before the temperature of 725°C is reached.

5.2.6 Modeling:

5.2.6.1 Drying section:

The modeling of drying is of little interest for the industry since in most spent potliners treatment applications they are generally pre-dried with fume gases, before being thermally treated. A simple one reaction model was used to describe the results. (Madhava et al., 2001; Freire et al, 1999).

$$\frac{dW_{H_2O}}{dt} = k_1 * \exp(\frac{-E_1}{RT}) * W_{H2O}^{n_1} \qquad (8)$$

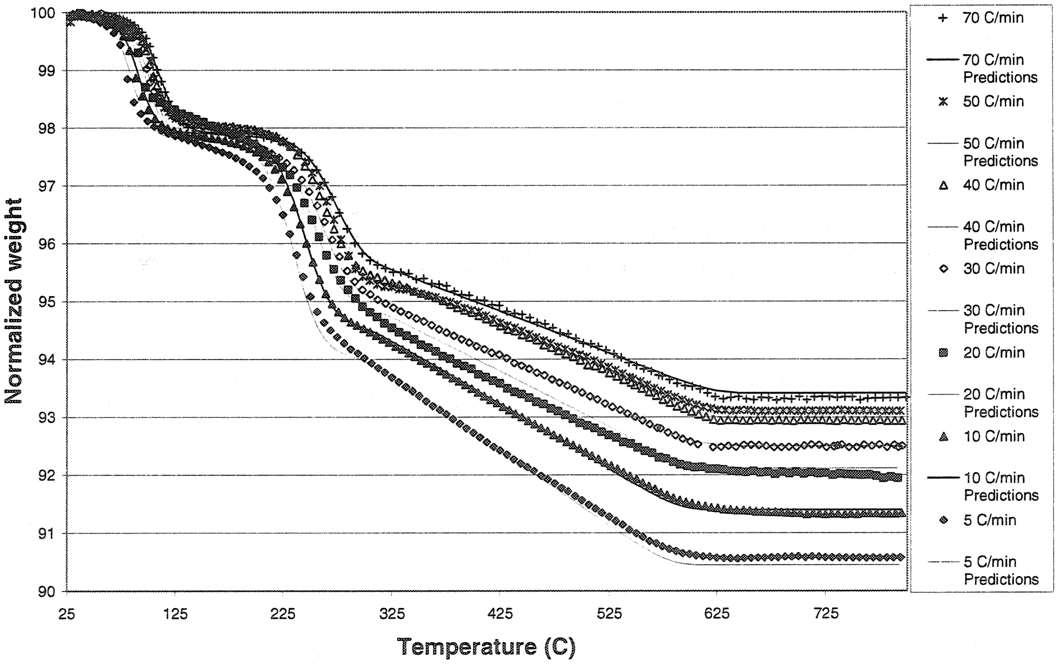


Figure 5.8: Experimental results compared to predictions for 7 heating rate in the case of the pyrolysis of spent potliners in an Argon atmosphere. (Note: the number of points used for this graph was reduced in order to make the figure readable).

The best fit for the parameters E_1, k_1, n_1 for all the experiments can be found in table 5.2a.

Table 5.2a: Kinetics parameters found in this study.

Parameters	**Value**	**Number of points fitted**
Drying		
k_1	$2.27*10^{13}$ s^{-1}	Ranged from 85-1200. Total: 2355
E_1	105 kJ/mol	
n_1	1.75	
Devolatilisation		
k_2	$2.86*10^{3}$ s^{-1}	Ranged from 145-2040. Total: 4004
k_3	$1.01*10^{6}$ s^{-1}	
E_2	90.1 kJ/mol	
E_3	105 kJ/mol	
n_2	1.62	
n_3	1.58	
Coking		
k_4	$5.18*10^{21}$ s^{-1}	Ranged from 85-1200. Total: 7302
k_5	$7.77*10^{14}$ s^{-1}	
E_4start	258 kJ/mol	
E_4finish	397 kJ/mol	
E_5start	193 kJ/mol	
E_5finish	298 kJ/mol	
Combustion Solid(2)		
k_6	$247*10^{6}$ s^{-1}	Ranged from 235-3300. Total: 6477
E_6	160 kJ/mol	
n_6	1.96	
Combustion Solid(3)		
k_7	$42*10^{6}$ s^{-1}	
E_7	146 kJ/mol	
n_7	1.53	

Table 5.2b can be used to compare the scant results available on the literature and related to other type of material. The quality of the fit can be verified on figure 5.8 and 5.9. The fit is reasonable but could be improved by using more complex model such as a distributed activation energy model (DAEM). However this type of model was not considered further because of the lack of interest of drying in the design of spent potliners treatment industrial units and a willingness from the authors to keep the total number of adjustable parameters to a minimum.

Table 5.2b: Kinetics parameters found in the literature for other types of material for comparison purposes.

Reference	Activation Energy (kJ/mol)	Preexponential factor (s^{-1})	Order of reaction	Material
Drying				
Pinheiro et al. (2002)	53.78-61.70	$3.7*10^5$-$3.4*10^6$	Assumed 1	Eucalyptus
Devolatilisation				
Kocaefe et al. (1995)	61.8 - 238	0.646-$2.12*10^{10}$	Assumed 1	Electrodes (gaz emitted)
Tremblay et al. (1988)	40-112	$2.40*10^5$-$4.6*10^9$	0.7-1.1	Electrodes
Sharma et al. (1999)	72.5 - 97.1	$3.7*10^5$-$1.3*10^9$	1.5	Rice husk
Mansaray et al. (1999)	142-188	$10*10^{15}$-$73.2*10^{17}$	0.7-0.8	Rice husk
Second devolatilisation / Coking (DAEM Model)				
Liu et al. (2001)	150-500	N.A.	Assumed 1	Coal
Maki et al. (1997)	150-400	10^{12}-10^{25*}	Assumed 1	Coal
Miura et al. (2001)	200-400	10^{10}-10^{25*}	Assumed 1	Coal
Gabor et al. (2002)	150-225	$10^{9.74}$-$10^{10.82}$	Assumed 1	Coal
Combustion				

Mc Donald et al. (1989)	95-115	N.A.	N.A.	Char
Patel et al. (1988)	76-120	N.A.	n_{O2}= 0.4-1.1	Char
Janse et al. (1998)	84.9-160	$5.3*10^5$	n_{O2}= 0-1 (0.74-0.82) n=0.49	Char
Branca C. (2002)	182.2	$1.10*10^{10}$	n=1.98	Treated Wood +minerals

* Preexponential factor depends on activation energy.

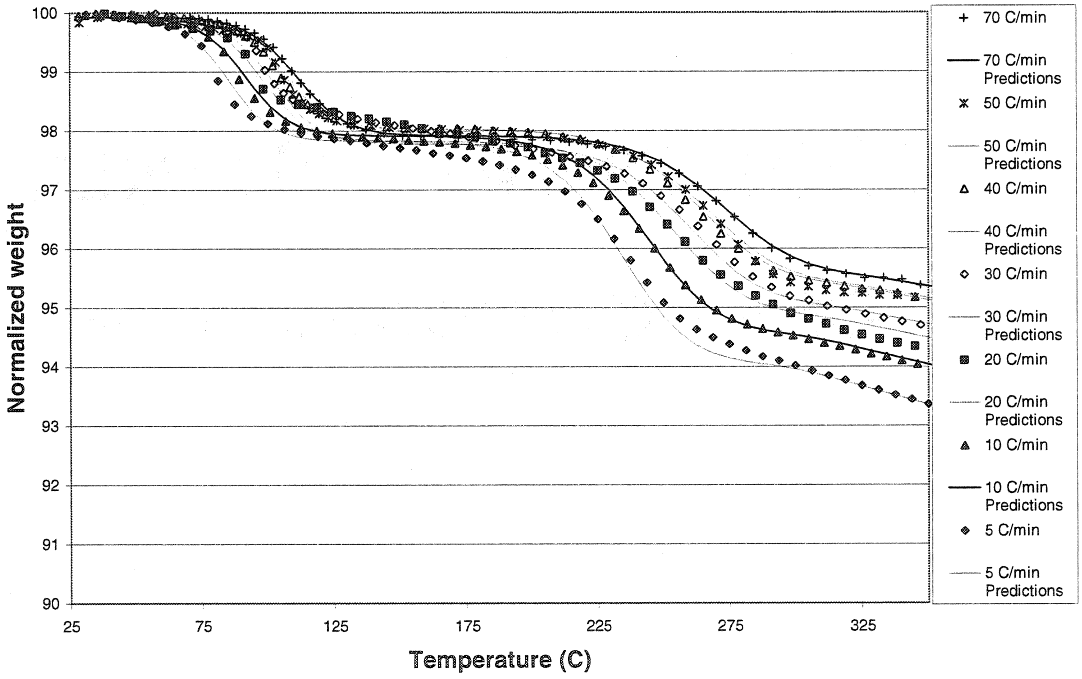


Figure 5.9: Zoom of figure 5.8 on drying and first devolatilisation and drying of spent potliners. (Note: the number of points used for this graph was reduced in order to make the figure readable).

5.2.6.2 First devolatilisation:

The first phase of devolatilisation is more interesting since it will be used to predict the amount of combustible gas that will have to be handled during the treatment of spent potliners. The devolatilisation takes place between 150°C and 320°C. It is characterized by a continuous decrease of the yields with respect to increasing heating rates, consequently it cannot be modeled by a single reaction where the ratio of gaz to solid obtained is constant (scheme 1, (Lee et Beck, 1984)).

$$\text{Solid (1)} \longrightarrow \text{Solid (2)} + \text{Gaz (2)}$$

scheme1

A better adapted scheme of reaction must be found in order to obtain a reliable 'Lumped kinetics model', (Salvador et al, 2003).

In more advanced models of biomass devolatilisation, the evolution of the yield was represented by scheme similar to scheme (2) (Koufopanos et Papayannakos, 1991).

$$\text{Solid (1)} \longrightarrow \gamma\,\text{Solid (2)} + (1-\gamma)\,\text{Gaz (2)}$$

Scheme 2

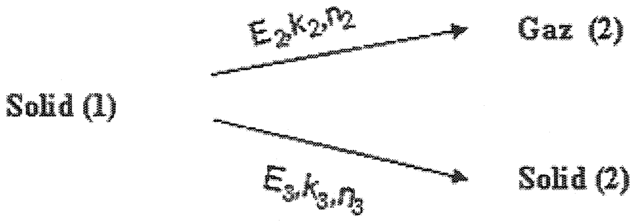
The coefficient γ being an empirically determined coefficient, dependant of the reactions conditions and whose variations is often attributed to secondary reactions taking place inside the sample and thus, is strongly dependant of mass transfer limitations.

This type of scheme (2) is not satisfactory in our study for two reasons:

- Figure 5.1-5.4 proves that mass transfer limitations do play an active role in the mechanism of the reaction.

- The coefficient γ is determined empirically and cannot be used to extrapolate predictions.

As a result scheme (3) was selected because of its ability to predict a change of yield with a change in the heating rate (Conesa et al.):



Scheme (3)

Both competitive reactions are characterized by kinetics constants, activation energy and order of reaction k_2, k_3, E_2, E_3, n_2, n_3,. Table 5.2a summarizes the results of the fitting process and figure 5.9 illustrates the quality of the fit. Table 5.2b shows that the parameters obtained are within the range found in the literature with other types of materials.

5.2.6.3 Second devolatilisation or cokefaction:

The second devolatilisation is characterized by a linear decrease of the sample weight starting at temperature 300°C and ending at 570°C (figure 5.6). The yield of the reaction is slightly different depending on the heating rate and can be seen in table 5.3.

The slopes of the linear section of the weight loss are compared for different heating rates as well in the same table. The slope of the curves obtained is very little dependant on the heating rate. A factor 1.8 exists between the lowest and highest slope measured when calculated with respect to the temperature, whereas a factor of almost 8 exists when these slopes are calculated with respect to time. In typical kinetics studies, reactions rates are supposed similar if temperature and conversion are similar. This is not the case here. Furthermore, the kinetics seems to start and end at well defined temperatures rather than a residence time.

This type of behaviour has not been modeled elsewhere in the literature, even though, it is quite commonly found in studies related to TGA studies pyrolysis reactions. Most studies dealing with complex devolatilisation reactions report experimental results showing a section of linear weight loss at the end of the reaction. This section is ignored by most models as being of very little importance to the final reaction yield (Calahorra et al, 1989; Zulfiqar et al., 1994; Aggarwal et Dollimore, 1997; Si-Dong et al., 2000; Tremblay et Charette, 1988;). It appears in our study that this section represent about half of the weight loss related to devolatilisation instead of the usual 5% reported in other studies. Consequently it cannot be ignored.

Table 5.3: Devolatilisation rate and yield for the second devolatilisation reaction.

Heating rate (Celsius/min)	Devolatilisation rate using 70°C/min as a reference.		Yield (%) (Carbon / Initial Solid content)
	Per time(min)	Per Celsius	
70	100	100	92.2
50	84	118	91.98
40	72	126	91.06
30	55	129	90.65
20	42	147	89.61
10	22	158	87.84
5	13	187	85.01

Studies carried out on the initial treatment of carbon to obtain the cathode used for the electrodes show a similar trend of linear weight loss past the initial devolatilisation. This behavior is associated with the coking of the samples. [Wilkening, (1983); Wallouch et al, (1972); Tremblay et Charette, (1988); Kocaefe and al., (1995); Shucker (1983)].

Consequently in order to take into account the fact that the reaction is strongly dependent on temperature, a model involving a very large distribution of high activation energy is be used. This model is ideally suited in this situation, because it predicts the fraction of solid that requires a minimum level of temperature before it can react. It has been widely used in the description of very complex reaction such as the one encountered in the pyrolysis of fossils fuels. The main difficulty of this type of model lies in the determination of the function of distribution of activation energy f(E), which represents the proportion of solid presenting a certain activation energy E, as well the preexponential factor distribution $k_0(E)$:

$$x = 1 - \int_0^{\infty} \exp(-k_0(E) \int_0^{t} \exp(-\frac{E}{RT})dt \bullet f(E)dE \tag{9}$$

With f(E) verifying the following equation :

$$\int_0^{\infty} f(E)dE = 1 \tag{10}$$

Finding the function f(E) and $k_0(E)$ is an exercise presenting great mathematical difficulties (Please et al., 2003). In order to do so, many approaches have been developed by various researchers (Liu et al., 2001; Maki et al., 1997). The most common approach is to assume the form of the functions f(E) and $k_0(E)$. Very often k_0 is considered constant, whereas f(E) is attributed a Gaussian form (Anthony and Howard, 1976; Maki et al, 1997).

$$f(E) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[\frac{(E-\overline{E})}{2\sigma^2}\right] \tag{11}$$

This simplification is not always suitable and other distribution of activation energy allow a better description of the reactions observed (Caballero et al, 1995). It cannot be used to describe a linear weight loss as observed in this study, since a Gaussian distribution of activation energy would result in a central peak in the range of temperature studied.

As this is not the case, the function f(E) has to be determined experimentally while some assumptions are taken as to the form of the function. For large values of activation energy, the preexponential factor will change very fast with respect to the temperature. It becomes then possible to assume that each reaction at particular activation energy can be considered as a step reaction (Please et al. 2003). When temperature is kept low, the degradation reaction of a particular fraction presenting activation energy (Es) does not take place, because the activation energy is too large. Once a trigger temperature (Ts) is reached, the reaction takes place almost immediately and the reaction rate observed is considered the result of the summation of individual steps functions (Caballero et al, 1995). This simplification is gaining acceptant in the analysis of non-conventional reaction rate (Liu et al., 2001; Maki et al., 1997).

In the case of this study, as the heating rate is linear with respect to temperature, the step function simplifications implies that the same amount of solid reacts when the temperature increase by ΔT whatever the initial temperature is between 300 and 570°C. Consequently, the distribution of activation energy was supposed flat, in other words, the cumulative distribution of solid fraction is linear with respect to the activation energy. This assumption of distribution of Activation Energy might seem original but close to flat distribution energy functions f(E) have already been reported in the literature (Maki et al, 1997).

The order of reaction is set to 1 as generally accepted for a reaction between gas and solid (Caballero et al., 1995).

The experimental observations have been interpreted in terms of two mechanisms (See figure 5.10):

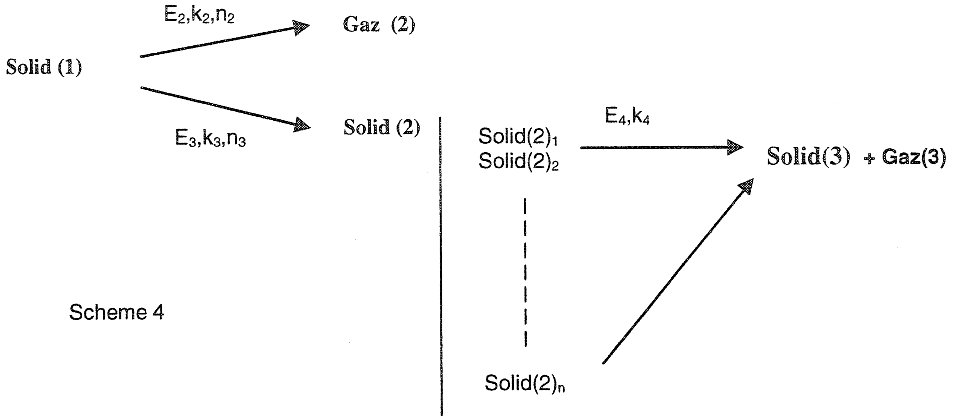
- It could possibly correspond to the traditional interpretation of the DAEM model (Scheme 4). A reaction, at a particular temperature between 300°C and

570°C corresponds to the degradation of a few molecules having a particular molecular weight and configuration which results in a particular Activation Energy different from other fraction of the sample undergoing the same reaction.

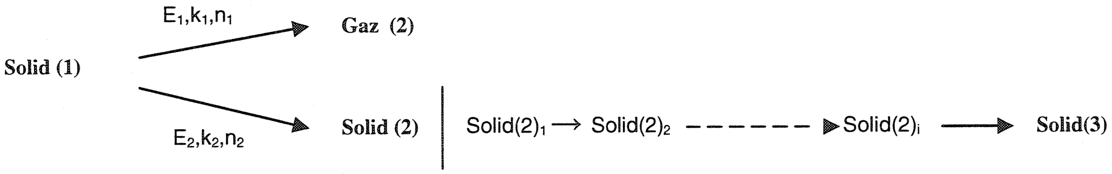
- It could be related to the depolymerisation of char each degradation yielding the material for the next one to take place at higher temperature. (Scheme 5).

Even though scheme 5 provides an elegant explanation for the linearity of the weight loss observed, a literature search showed that this scheme was highly unlikely [Fish et al., (1995); Raihane et al., (1994); Li et al., (1999), Knuemann et al. (1991), Caloharra et al. (1989)]. The degradation of polymers yields shorter polymers chains, and these new piece of polymers are more easily degradable than the initial molecules [Caloharra et al, (1989)]. Consequently, once the degradation starts, it accelerated and is terminated over a very narrow range of temperature. As a result, depolymerisation mechanism was not considered and a traditional DAEM interpretation was used.

However, an additional aspect of this reaction is that fact that the yield of the reaction is changing from 92 % solid at 70°C/min, to 85 % at a heating rate of 5°C/min.



Scheme 4



Scheme 5

Figure 5.10a: Possible reaction scheme explored in the case of the linear section of the devolatilisation.

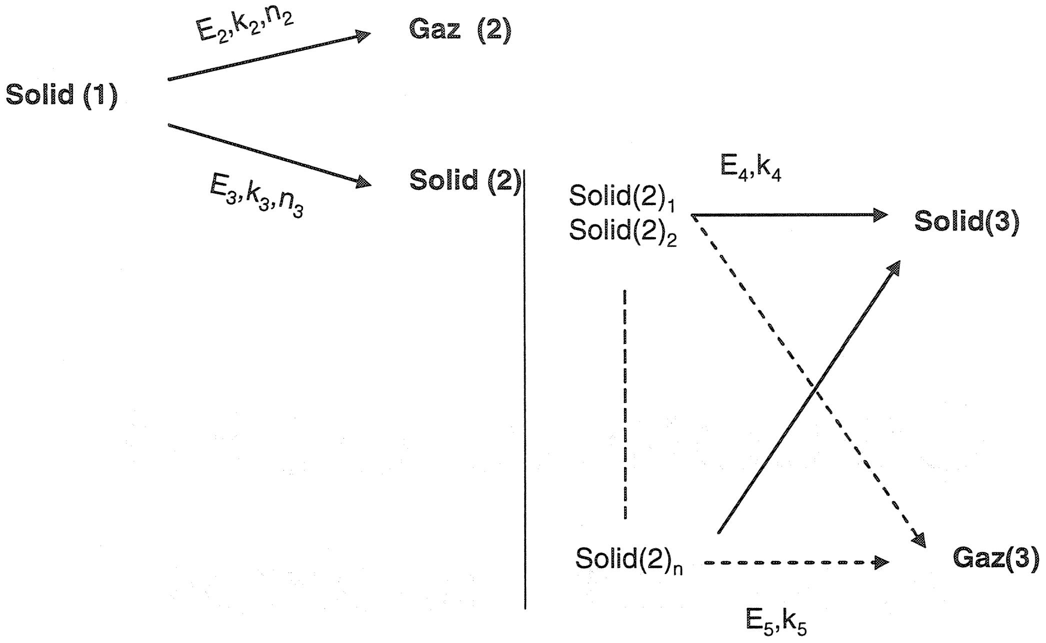


Figure 5.10b: Reaction scheme 4 with parallel reactions used for the modeling of the linear section of the devolatilisation.

Consequently, scheme 4 of figure 5.10a cannot be used to adequately represent the weight loss observed. The change of yield can be explained only by two mechanisms:

1) The existence of secondary reactions.
2) The existence of competing reactions.

Mechanism 1) is highly unlikely, since secondary reactions would be dependant on the concentration of gas in the crucible, which itself is strongly dependant on mass transfer limitations. Since mass transfer limitations are inexistent, in the configuration selected for this study, a secondary reaction does not explain the change of yield.

Consequently, a competing reaction was selected as the best model capable of representing the experimental results observed [Conesa et al, (2001), Gabor et al. (2002)].

Both competitive reactions are characterized by kinetics constants, and range of activation energy k_4, k_5, E_4start, E_4finish, E_5start, E_5finish. (See figure 5.10b).

5.2.6.4 Combustion:

A lumped kinetic approach was used to model the combustion. When combustion starts, two types of material are susceptible to burn: Solid(2) and Solid(3).

Solid(3) combustion kinetics can be obtained by measuring the combustion rate beyond 650°C after devolatilization has ended and Solid(2) disappeared. By using the derivative based method outlined by Haines (1995), kinetics parameters have been estimated for heating rates ranging from 20 to 70°C per minute. Kinetics data could not be obtained for experimental results 5°C/min, as the reaction is almost completed when the temperature of 650°C is reached. The kinetics parameters (E6, n6, k6) found were then optimized by fitting. They are summarized in table 5.4.

Table 5.4 : Kinetics parameters for the combustion of Solid(3).

Heating rate (Celsius/min)	Activation Energy found (kJ/mol)	Order of reaction	Ln(Preexponential factor)
20	148	1.53	22.9
30	147	1.53	22.6
50	143	1.53	22.1
70	142	1.53	21.8
Fitted parameters for the 5 to 70°C/min	143	1.539	22.65

Table 5.5: Kinetics parameters for the combustion of Solid(4)=Solid(2)+Solid(3).

Heating rate (Celsius/min)	Activation Energy found (kJ/mol)	Order of reaction	Ln(Preexponential factor)
5	96	1	15.37
20	95	1	15.44
30	96	1	15.46
50	95	1	15.43
70	97	1	15.63
Fitted parameters for the 5 to 70°C/min	96.2	1	15.47

Four models have been tested in order to compare their ability to predict the combustion behavior of spent potliners over the full range of combustion temperature at four different heating rates (see figure 5.12):

a) Solid (2) does not undergo combustion only Solid(3) burns. The kinetics parameters for this reaction can be found in table 5.4.

b) Solid (2) undergoes the same reaction than Solid(3) but separately. The kinetics parameters found in table 5.2) are used for both solids.

c) Solid (2) and (3) undergo the same reaction of combustion. For this analysis, a new specie Solid(4) was artificially defined as consisting of the sum of Solid(2) and Solid(3). The kinetics parameters of the combustion reaction was found by applying the derivative methods described by Haines et al. (1995) on the FULL range of combustion temperature (450-800°C). The kinetics parameters found are summarized in table 5.5.

d) Solid (2) undergoes a separate reaction of combustion. The kinetics parameters for this reaction are found by fitting the predictions to the experimental results.

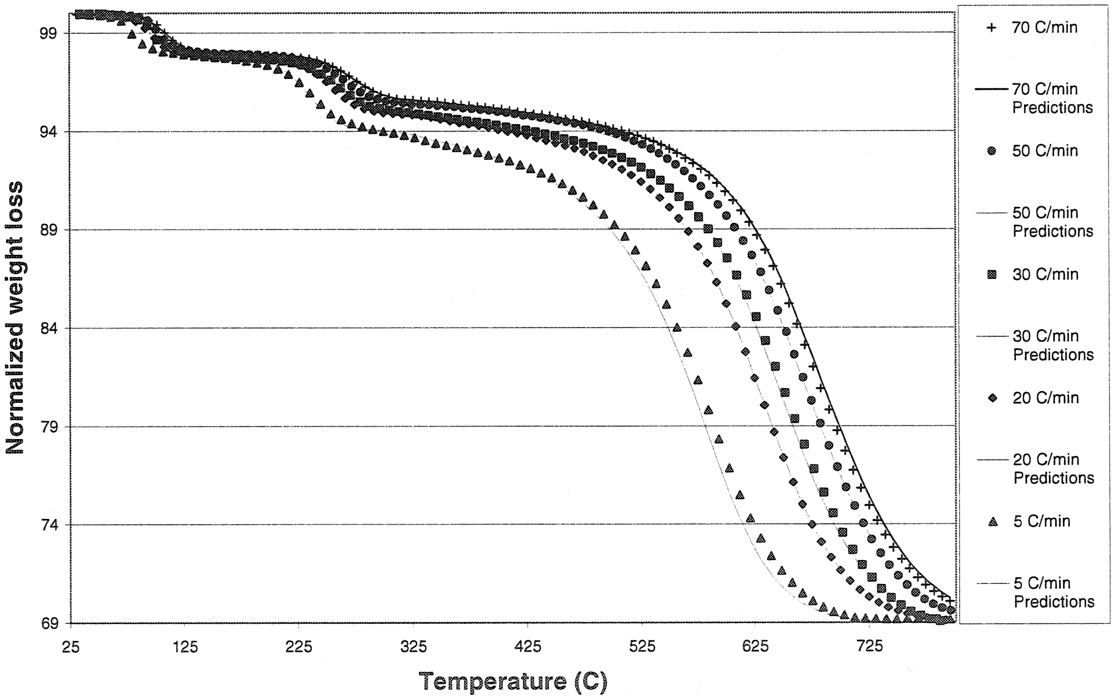
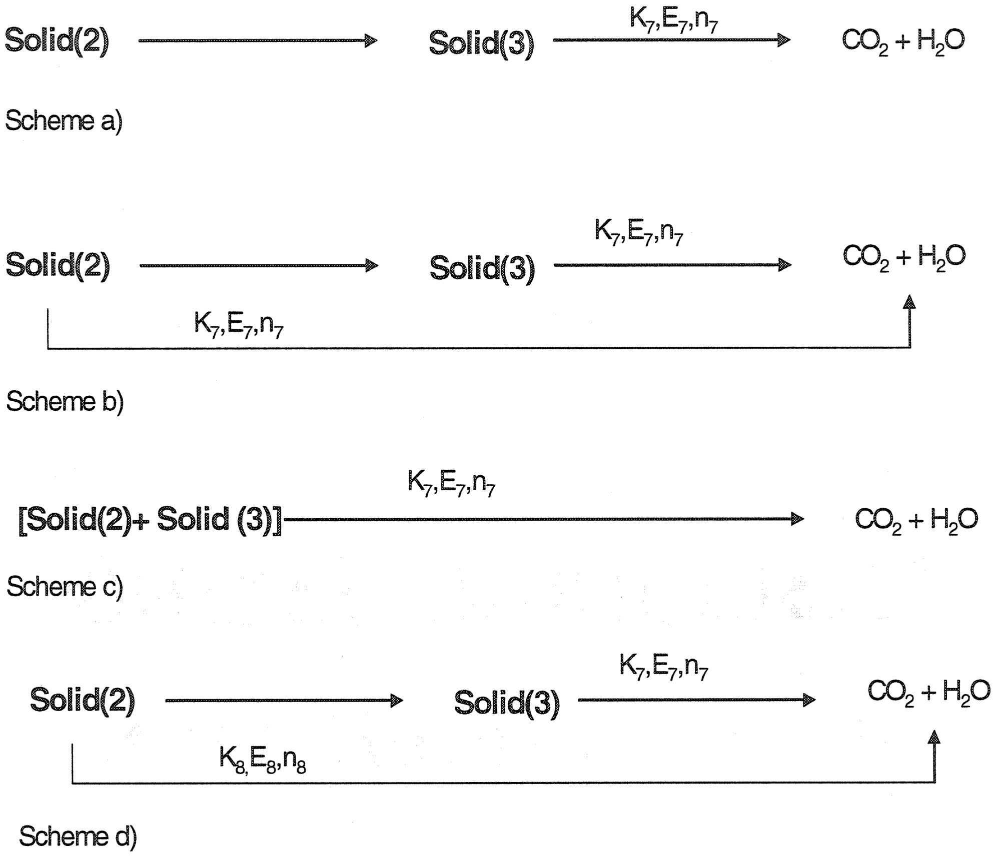


Figure 5.11: Comparisons of d) model predictions with experimental results for combustion.



Scheme a)

Scheme b)

Scheme c)

Scheme d)

Figure 5.12: Various mechanisms tested to model the combustion of spent potliners.

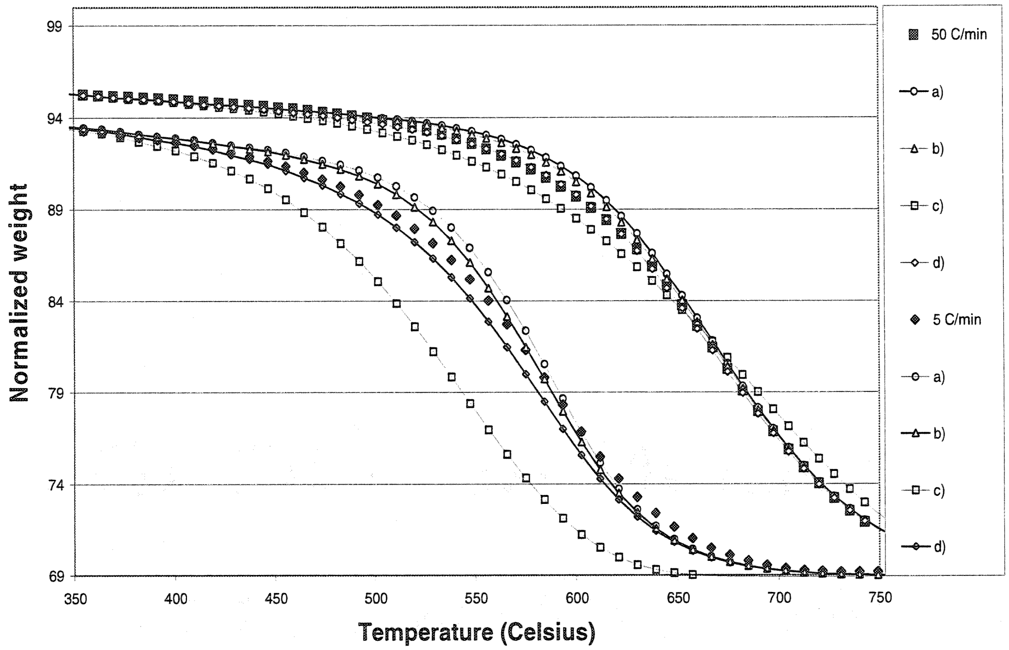


Figure 5.13: Comparisons of combustion experimental results to predictions according to the model used (discrete points: experimental data, linked points: model).

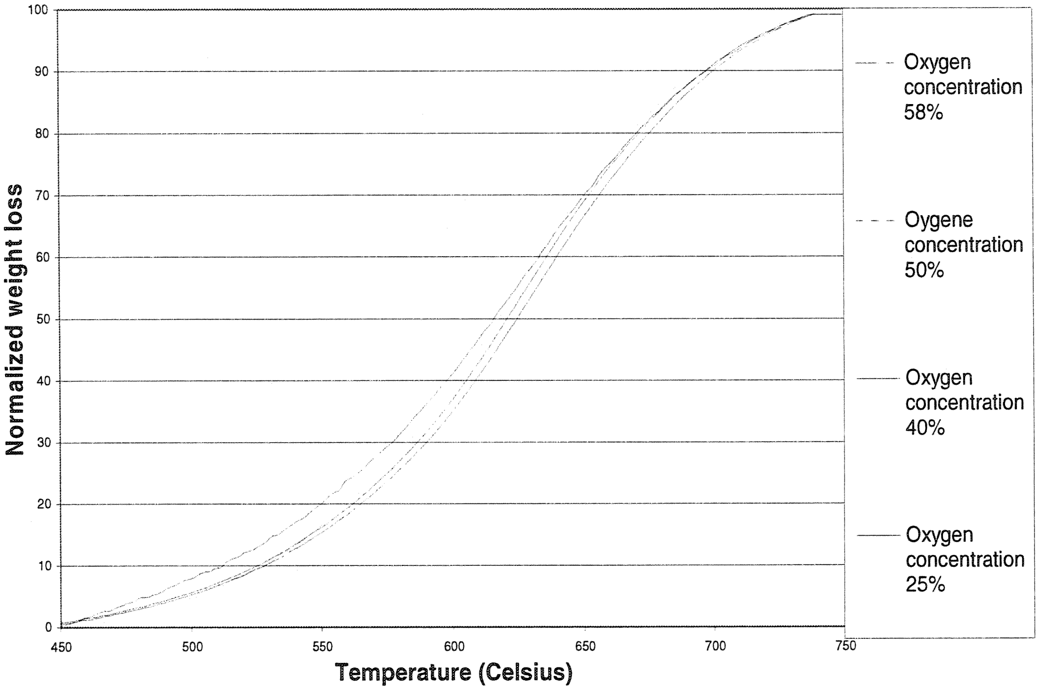


Figure 5.14: Effect of oxygen concentration on the combustion of 45-75 microns particles at 20°C/min.

Configuration a to d) were thorough fully investigated for all heating rates. Figure 5.13 illustrates the results obtained for the 5 and 50°C/min case.

Each configuration could be used to perfectly fit the results at one particular heating rate, but the same kinetics parameters could not fit the results at other heating rates. Only configuration d) could predict accurately the combustion of spent potliners using the same kinetics parameters for each heating rates.

This study illustrates the theoretical work of Wilburn (1998,2000), which showed that two reactions taking place at the same time could be modeled by a single set of kinetics parameters, however these parameters did not remain constant when the heating rate is changed.

The kinetics parameters related to the combustion of Solid(2) or precarbonized carbon were obtained by fitting the predictions to the results yielding the values of kinetics parameters (E3, n3, k3).

Configuration d), lead to predictions presenting an error on average of 0.8 % (see equation (7)). The parameters obtained can be found in table 5.2.

Oxygen effect:

The effect of oxygen concentration was studied by increasing the oxygen content of the furnace by up to four times. Janse et al. (1998), explains that the order of reaction for the oxygen range from zero at low temperatures to 1 depending on which reaction is rate determining. Bopp et Brupbacher (1985) explains that in gas solid reaction, if the surface of the solid is saturated with reactants, it is common to observe order zero reaction. Figure 5.14 presents the results obtained for 45-75 microns particles and at a heating rate of 20°C/min. Varying the oxygen content does not have a significant effect on the reaction kinetics; consequently the order of oxygen was approximated to zero. The value calculated by fitting corresponded to a value of 0.07.

5.2.7 Conclusion:

In this article, the pyrolysis and combustion kinetics of spent potliners were investigated using a TGA. Mass transfer limitations were alleviated by limiting the particles size to diameters of less than 125 microns, sample size reduced to less than 5 mg sample. Heat transfer limitations were minimal for heating rates in the range of 30 to 50°C/min and considered negligible from 5 to 70°C/min. The pyrolysis can be described by three stages: drying, devolatilisation and coking. Drying was modeled by a single reaction mechanism; devolatilisation was modeled by a two competitive reaction model, whereas coking modeling was realized by using two competitive reactions with a distribution of activation energy. Combustion was studied in the low temperature range (500-800°C) and is best modeled by using a two reaction modeled representing the combustion of unreacted carbon and coke. The predictions of the model were validated for heating range varying from 5 to 70°C/min, with constant kinetics parameters. The average error is less than 0.24%.

5.2.8 Acknowledgements:

We would like to acknowledge the financial support of Polysolutions, inc.

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CHAPITRE VI :

CARACTÉRISATION DE L'ADSORPTION DES FLUORURES SUR LES PARTICULES DE BRASQUES.

6.1 Présentation de l'article.

Les deux chapitres précisent les conditions de traitement du cyanure des brasques. Le deux chapitres suivants sont consacrés au traitement des fluorures des brasques.

Dans une première étape les caractéristiques de la lixiviation des fluorures des brasques sont étudiées. Le chapitre 6 est constitué de l'article intitulé **'Spent potliners fluoride adsorption characterisation'** soumis pour publication à la revue **Separation and purification technology**. L'objectif de ce chapitre est d'étudier les caractéristiques de lixiviation des brasques. Les effets de la température, agitation, pH ont été mesurés. À partir des données obtenues, un mécanisme de réaction de lixiviation a été posé impliquant, la dissolution des fluorures et leurs adsorptions à la surface des particules de brasques. En se basant sur ce modèle, une isotherme de Langmuir a été utilisée pour modéliser les résultats obtenus. Les effets de deux solvants sont étudiés: de l'eau acidifiée et une solution contenant 120 g/L de sels de Na_2SO_4. Cette deuxième solution correspond à de l'eau de procédé recyclé tel qu'expliqué au chapitre 7.

6.2 Spent potliner fluoride adsorption characterisation.

Référence: Yann Courbariaux, Jamal Chaouki*, Christophe Guy. (2004) : 'Spent potliner fluoride adsorption characterisation'. Submitted to Separation and Purification Technology.

Keywords: Spent potliner, fluoride, leaching, process modeling, Aspen, sorption, Langmuir.

6.2.1 Abstract:

Spent potliners are a by product of the aluminium industry. It is considered a hazardous waste, in part, because of its leachable fluoride content. The leachable fluoride content can be removed by washing. The present study investigates the leaching and adsorption of fluoride by spent potliner in the case when acidified water and a 120 g/L Na_2SO_4 are used as leaching solutions. A mechanism is suggested to describe the fluoride leaching reaction observed involving three steps: dissolution of NaF, adsorption of fluoride, and potential precipitation of fluoride ion. The amount of fluoride adsorbed is independent of the pH of the solution and decrease along with an increase of the temperature. A Langmuir isotherm was used to model the adsorption. High sulphate concentrations seem to activate the adsorption phenomenon. The results obtained are used to show that water involved in a spent potliner leaching process must be recycled.

6.2.2 Introduction

Spent potliner (or SPL) represents a disposal issue aluminium producers worldwide have been faced with for years. For the Quebec province alone, in excess of 50 000 tons of spent potliner are generated yearly. Most of these 50 000 tons is not disposed of, and is stored in dedicated warehouses awaiting suitable treatment. A similar situation prevails in the US where, since 1998 landfill of spent potliner is forbidden by the E.P.A. (Environmental Protection Agency).

Spent potliner originates from the disposal of the carbon cathodes used in the process of aluminium production. Details about the origin and content of spent potliner can be found in an article by Pawlek, (1993). They are considered a hazardous waste for two main reasons: high cyanides content, and high fluoride content. An exhaustive description of the issue of cyanides treatment has been dealt with in another article (Courbariaux et al., 2004a). They can be easily destroyed by partial combustion. This article will only focus on fluoride treatment of the residue obtained after destruction of the cyanides.

Fluoride is reported to be found naturally in spent potliner particles either as sodium fluoride (NaF) or cryolite (Na_3AlF_6) (Brown and Reddy, 1994). However, the occasional presence of other species has been referenced: Grolman et al. (1994) reports that at high temperature and in the presence of lime and sand, fluorosilicate such as cuspidine ($Ca_4SiO_7F_2$) can be formed and this compound is soluble in alkali conditions.

Upon storage of spent potliner, sodium fluoride salts are easily dissolved by rainwater and can contaminate local runoffs in concentration ranging from 0.1 to 8.5 g/L (Pawlek, 1993). The US TCLP is the most commonly used method to evaluate the leaching properties of the fluoride content of spent potliner. It consists in contacting spent potliner with an acid buffer solution in a ratio 20:1. The main difficulty of this method lies in the fact that spent potliner are a basic residue (Silviera et al., 2000), consequently, when mixed with acid, the resulting solution will present a neutral pH. Personnel et al. (1987) showed that fluoride leaching in spent potliner is minimal when solutions with pH close to neutral are used. However in natural conditions, rain contacting non-neutralized spent potliner results in a basic solution which leads to optimal conditions for the dissolution of fluoride. Therefore the EPA recommended the use of distilled water instead of an acid buffer solution in a modified TCLP procedure in order to correctly evaluate the leaching ability of fluoride in spent potliner. (Chanania et Eby, 2000).

Fluorides have to be removed from spent potliner before a definitive disposal solution can be found. This can be done by washing spent potliner till leachable fluoride concentrations in residues are below legal regulations for industrial liquid waste streams ranging often from 50 to 150 ppm. This work is part of a major study aimed at designing a leaching process of spent potliner (Courbariaux et al., 2004b). As a result, it is necessary to study the release of fluorides in spent potliner in order to properly design a washing process. NaF are readily leachable salts and relatively highly soluble (41 g/L), so one wash could be potentially enough. However it is well known that fluorides are easily adsorbed on a wide variety of materials. This potential for adsorption could increase the number of washes necessary for complete removal of leachable fluoride salts.

Extensive studies related to fluoride adsorption can been found in the literature. However they are all related to low concentration adsorption and the possibility of making fluoride contaminated water safe to drink. A few aspects are common to all fluoride sorption studies: effect of pH and temperature on adsorption, kinetics of reaction and type of model used to predict adsorption.

Lai and Liu (1996) studied the adsorption of fluoride on spent catalyst used for hydrocarbon cracking in refineries. The fluoride concentration studied ranged from 0.02 to 0.04 g/L. They report finding increased adsoption by a factor 4 between pH=1 and 9. The temperature was varied from 5 to 50°C and they reported a slight increase in fluoride particle loading with an increase of temperature. This behaviour is associated with an endothermic adsorption reaction. Their kinetics study shows that within 10 minutes, 70% of adsorption has taken place. A linear adsorption model was used to describe the adsorption isotherms. Finally, their findings attribute the adsorption properties of spent potliner to the formation of fluoro-alumino complex and the driving forces of adsorption to Coulombic forces.

Cengeloglu et kir (2002) used red mud, a by-product from the extraction of alumina from bauxite to adsorb fluorides. The maximum concentration of the fluoride solutions used was 0.0456 g/L. Adsorption was shown to slightly increase between pH 1 to 5, but sharply decreases between pH of 5 and 10. A contact time of 120 minutes was used to make sure that the reaction was completed before analysis took place. Either a Langmuir or Freundlich isotherm model could be used to describe their results.

Sinha et al. (2003) used the carbonized form of water hyacinth called 'Eichhornia Crassipes'. Their studies focused on a range of fluoride concentration varing from 0.002 to 0.025 g/L. Temperatures were varied between 25 and 43°C and shown to boost fluoride adsorption. Six to eight hours were necessary for the equilibrium concentration to be reached. Only a Freundlich isotherm model could be used to describe the results.

Leyva-Ramos et al. (1999) studied the adsorption of fluoride on aluminum impregnated carbon. The range of concentration used varied from 0.0005 to 0.015 g/L. Adsorption was four times higher at pH 7 compared to pH 1. Experiments performed involved a contact time of 5 days and a Langmuir isotherm model was used to describe the experimental results.

Finally, Fan et al. (2001) studied the effect of adsorption for 4 types of material composed of hydroxyaoatite, fluorspar, quartz, calcite. The maximum concentration used was 0.0000634 g/L of fluoride. The reaction completion involved more than three hours of contact time for the hydroxyapatite, but less than two minutes for the others. Freundlich isotherms were used to model the results obtained.

In all the articles found the literature, fluoride adsorption is studied following the addition of sorbents to fluoride containing solutions. However in the present study, fluoride salts are initially contained in the spent potliner particles and end up in the solution after contacting the particles with water. So the conditions of adsorption are not as straightforward and well-controlled as in other studies. Moreover, the fluoride concentrations studied in the present article are more than a 100 times (5 g/L) higher than in any other study reported in the literature which makes fluoride concentration measurements easier.

This article focuses on the release of fluoride by spent potliner once in contact with water:

$$SPL + H_2 0 \rightarrow (F^-)_{aq} \qquad (1)$$

Two solutions will be used:

- A Fresh water solution acidified with sulphuric acid at pH 4,
- A highly concentrated sodium sulphate (Na_2SO_4) solution (120g/L) at pH 4.

Solutions of pH 4 were used in this study so as to mimic the conditions found in the leaching process being studied which itself reproduce the conditions found in TCLP measurements. The reason why highly concentrated sodium sulphate solutions are used lies in the fact the processes related to spent potliner washing will necessitate high quantity of water. This water should not be wasted, but recycled. The result of multiple recycling involving high quantity of sulphuric acid will be the concentration of sodium cations and sulphate anions. Consequently, in processes using recycled water, the spent potliner will be washed by highly concentrated sodium sulphate solution. (Courbariaux et al, 2004b).

The fluoride content of spent potliner was determined by using neutron activation analysis and was evaluated at 18.2 % by weight. The composition of spent potliner is highly variable. It is constituted of two fractions one carbonaceous and another composed of refractory. Variations in the quantity of these fractions explain the variability of the samples and the variability of their leaching characteristics especially when small sample sizes are used for the experiments. In the course of this study, fluorides concentration in sample was found to range from 17.2 % up to 19.2%.

The percentage of easily leachable fluoride was determined by leaching varying small sample size of spent potliner in a 2-liters solution of water so as to minimize adsorption and was found to stand at about 55%. The remaining fluoride is assumed to be locked in cryolite salts (Courbariaux et al., 2004b).

6.2.3 Experimental

It is important to study the kinetics of leaching to meet the double objectives stated below:

- Verify that that an equilibrium or pseudo-equilibrium can be reached.
- Estimate the effect of process parameters on the kinetics of reaction.

In any washing process, residence time of the particles in contact with the leaching liquid is unlikely to be higher than 60 minutes. If higher residence times were used the size of vessels used to handle significant quantities of spent potliner for prolonged period of time would be too high. As a result, adsorption reactions that can take more than a few days [Leyva-Ramos et al. (1999)] to reach completion are not relevant in the current study since completion will not be reached within only sixty minutes.

Kinetics are of a great importance in the design of reactors. In process engineering, a fast reaction is a reaction that is completed in well mixed vessels in less time than the time that is required for mixing in an industrial unit. So, reactions completed in less than a few minutes are considered immediate and to reduce further the residence time needed in the reactor, investments should be made on getting better mixing rather than accelerating kinetics.

6.2.3.1 Determination of the apparent leaching kinetics of spent potliner:

For every kinetics leaching experiments, a 50 g sample of calcined spent potliner is mixed in a 1-liter water solution, acidified with 8 mL of sulfuric acid. At regular times, a sample of the liquid was obtained, diluted from concentration in g/L to the 0.5-2 ppm measuring range and its fluoride content was analyzed with a Hatch spectrophotometer using a colorimetric method (SPADNS). This type of analytical method is very sensitive to interferences from other cations and anions when used to check drinking water standard. So the accuracy of the measurement was verified regularly by using various mixture of 1 mg/L fluoride standard solution and the solutions whose concentration was unknown. The results obtained showed that interferences were not detectable, and this is likely due to the high level of dilution involved in the measurements (up to 100 000 times) which likely inhibited the effect of any potential interferences. The values reported in this study represent the average of at least three measurements.

The release of fluoride in solution can be affected by three parameters depending on the limiting steps in reaction (1) mechanism:

1) Internal diffusion of the reactive or products of the reaction.

2) The intrinsic kinetics of the chemical reaction.
3) External diffusion of the reactive or products of the reaction.

In order to investigate which mechanism plays an important role, a series of experiments were performed:

6.2.3.1.1 Particle size reduction.

Experiments have been carried out with two particles size A and B. The particle A presents an average diameter three times the diameter of particle B. From the results obtained (figure 6.1), it can be concluded:

- Equilibrium or pseudo equilibrium is reached immediately for small particle size.
- Final fluoride concentration is not affected by the particle size.
- Smaller particles leach more rapidly than bigger particles.

As a result, it can be concluded that internal diffusion plays an important role in the kinetics of leaching for big size particles. If small size particles are used, the internal diffusion appears to be none controlling.

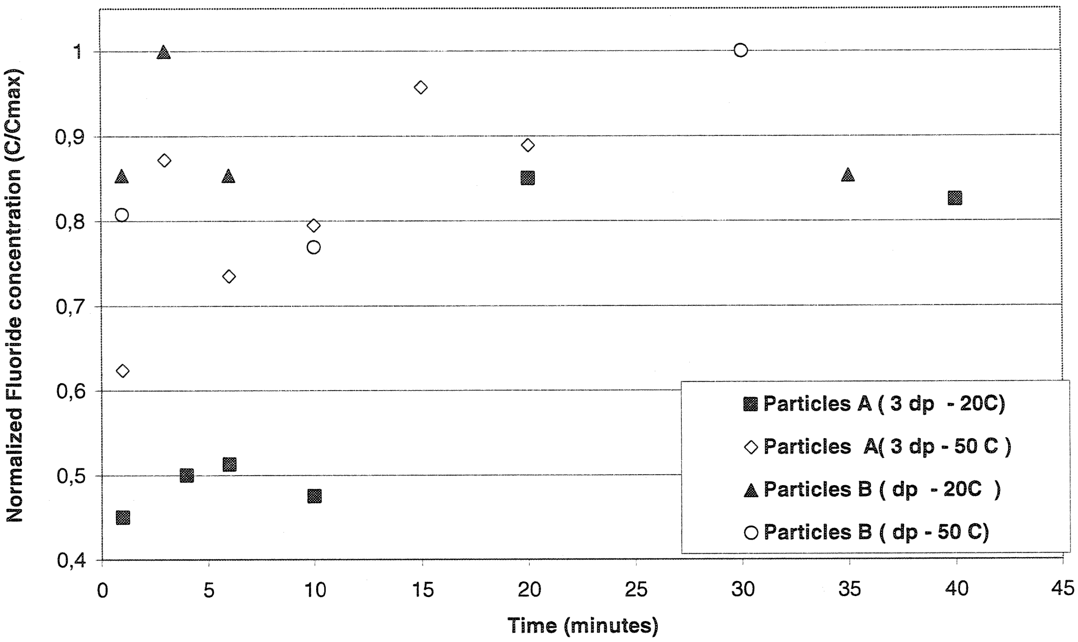


Figure 6.1: Particles size and temperature effects on the kinetics of leaching.

6.2.3.1.2 Temperature increase.

In order to verify the effect of the temperature, leaching experiments were carried out using the particle size A and B at 20 and 50°C (figure 6.1). No difference can be noticed in the apparent leaching kinetics for low particle size since the reaction is almost immediate in both conditions. However kinetics of leaching are increased for large particle size leached at higher temperatures. Since, the previous experiment had shown that leaching is controlled by particle diameter; higher diffusion rate are likely to be the reason behind increased kinetics rather than an increase in the intrinsic leaching kinetics.

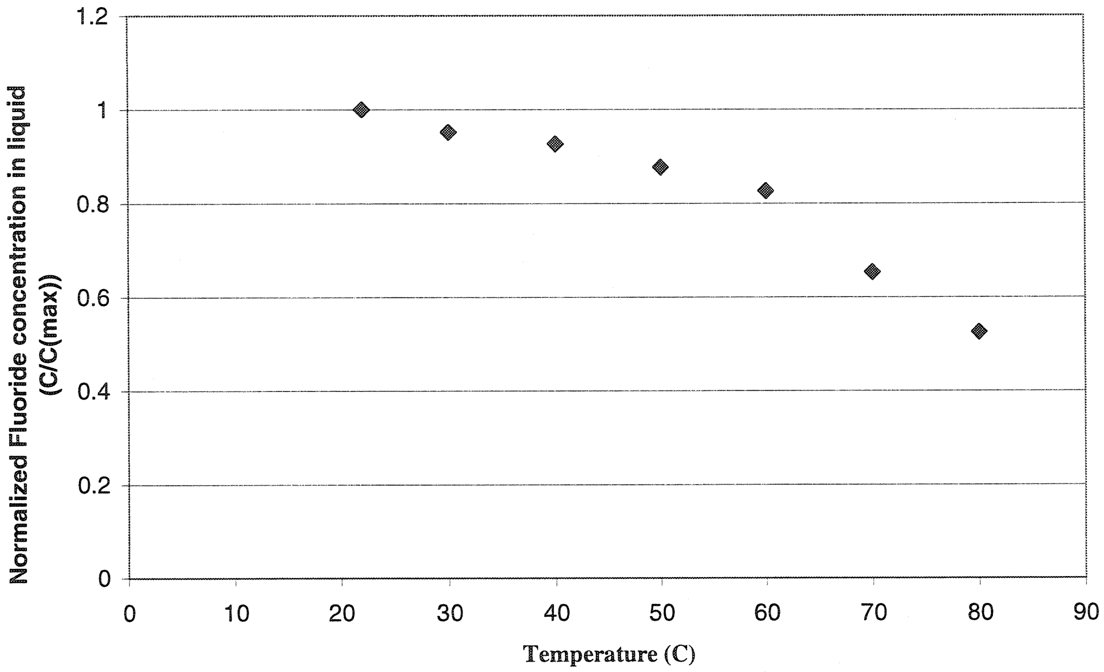


Figure 6.2: Effect of temperature on the leaching of fluoride.

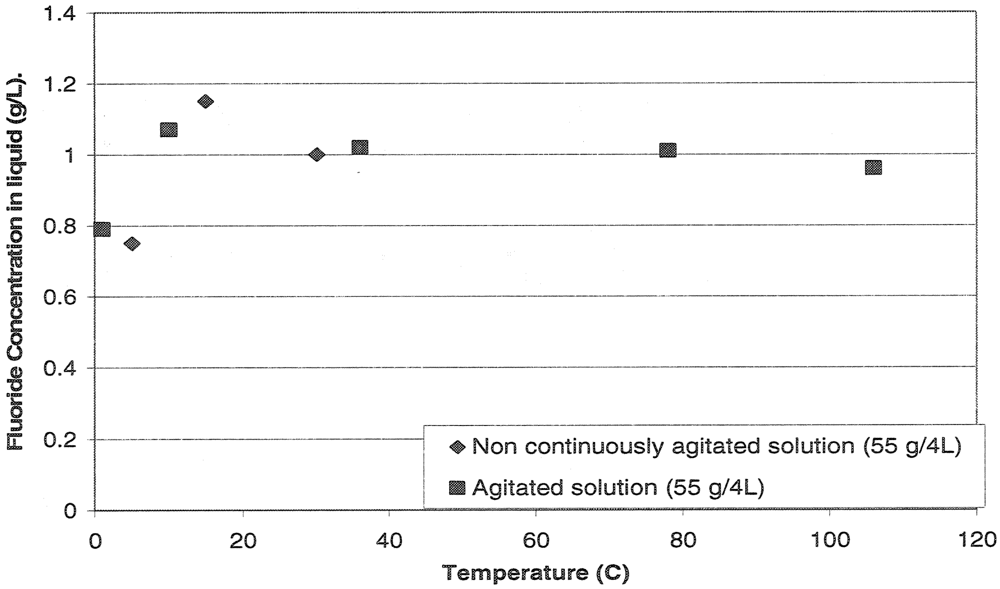
The effect of temperature on the final fluoride concentration has been investigated in second experiments whose results are presents on figure 6.2. The concentration of fluoride found in the liquid after reaching pseudo-equilibrium is decreased along with an increase of the temperature. The effect is particularly important at temperatures higher than 50°C.

These two observations will be important in the optimization of the leaching process. Lower temperature will increase the amount of fluoride leached, however it will decrease the kinetics of leaching through lower internal diffusion rate. The latter effect can be downplayed by reducing the particle size. Lower leaching temperatures reduce the heating costs, slower kinetics imposes high residence time for equilibrium to be reached which results in higher reactor volume, finally smaller particle size increases the cost related to particle crushing. On this basis, an optimum will have to be found to optimize these three factors.

6.2.3.1.3 Mixing rate

In order to characterize the effect mixing two experiments have been carried out with the smallest particle size:

The first one involved the comparison of the kinetics of leaching between a) an agitated vessels and b) a vessel agitated only for a few seconds till, visually, a good suspension was obtained and then the solution was let free to settle. Results are illustrated on figure 6.3a. Variation in mixing had little effect on the kinetics of leaching. Even though this type of experiment does not allow a full characterisation of the effect of mixing, the results obtained show that mixing has little impact on the leaching kinetics for small particles. These results confirm the previous conclusions showing that leaching of small particles is immediate with respect to mixing time.



Note: The experiment took place at a concentration of 13.75 g/L instead of 50 g/L.

Figure 6.3a: Mixing effect on the leaching of fluorides.

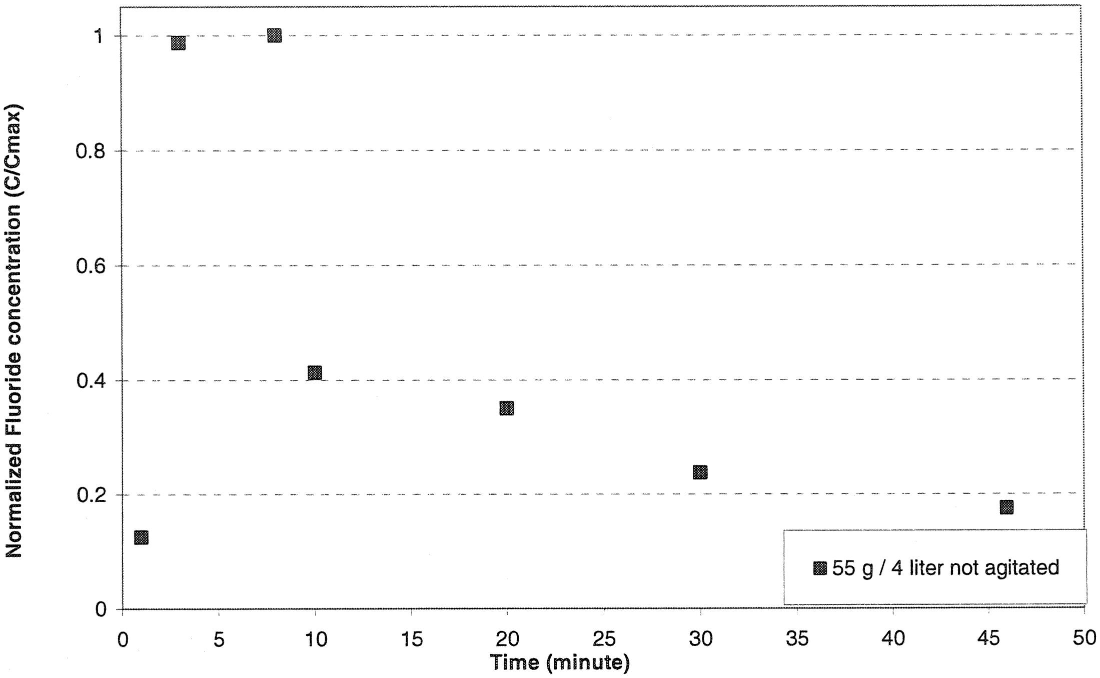


Figure 6.3b: Effect of settling on the fluoride concentration in liquid phase.

The second experiment was designed to characterize the effect of settling on the fluoride concentration in liquids (figure 6.3b). The fluoride concentration drops over time as spent potliner particles are settling. It seems that in the absence of agitation, fluoride attach themselves to the spent potliner particles, resulting in the gradual decrease of concentration in the liquid. This bonding of fluoride seems very weak since if spent potliner particles are put in suspension again; the fluoride concentration jumps back to pre-settling levels. (cf. table 6.1).

Table 6.1: Fluoride concentration measured in mg/L in precipitation experiment.

15 minutes mixing	Sampling after sedimentation (24 hours)		Sampling after sedimentation and mixing
1.08 mg/L	Bottom	Surface	1.10 mg/L
	0.28 mg/L	0.28 mg/L	

In conclusion to the results presented in the figures 6.1,6.2,6. 3:

- Pseudo-equilibrium is reached almost immediately for small particle size.
- The kinetics of leaching are controlled for big particles, by internal diffusion of fluoride. If small particles are used, mixing is likely the controlling factor.

Consequently, the particle size chosen for the rest of the tests was the smallest one.

6.2.3.2 Mechanism of reaction determination.

Even with the kinetics of the leaching reaction well controlled, the exact nature of the reaction described in (1) remains unknown. The natural explanation that should be considered first is that leachable fluoride from spent potliner results from the dissolution of soluble salts NaF (about 41 mg/L) present in spent potliner (Courbariaux et al, 2004b). In order to test this hypothesis, variable amounts of spent potliner were leached in both water and Na_2SO_4 solution and the fluoride concentration obtained experimentally was compared to the predictions obtained with a model assuming that all of the NaF is dissolved.

Experimentally the experimental procedure used to study the leaching reaction consisted in:

- Spent potliner and the leaching solution were contacted in a 1 liter beaker agitated with a magnetic stirrer.
- After 15 minutes, 10 mL of the solution was sampled and its fluoride content was analysed.

- The mixture was filtered using a buchner filter and a water vacuum pump. The filtration was performed three times to ensure complete separation.

The concentration of both the filtered solution and the 10 ml sample were compared to verify if fluoride adsorbed during filtration on the buchner filter and if fluoride precipitated in the 10 ml extract might affect the results. Both measured concentrations were found to be very similar (inferior to 10% difference), except at concentrations higher than 6 g/L which corresponded to only one experiment. The concentrations reported represent the average of both measures.

Figure 6.4 compares the experimental results obtained to the concentration that would be obtained if no adsorption was observed. Since NaF is readily leachable and the maximum concentrations found are about half of the saturation value (19 g/L) it is likely that the difference between solubility and observed results corresponds to adsorption.

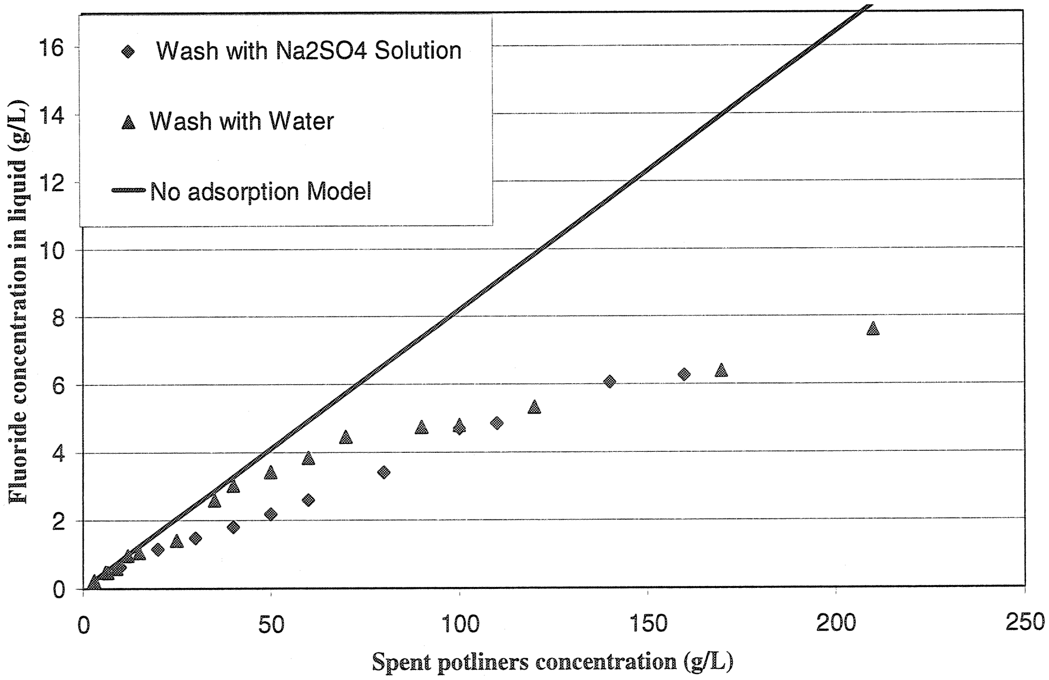


Figure 6.4: Comparison of ideal (no adsorption) and experimental concentrations of dissolved fluoride.

After taking into considerations all the results presented previously, the following mechanism of reaction in three steps is proposed:

$$(NaF)_{SPL} \rightarrow Na^{+} + F^{-} \qquad (2)$$

$$(F^{-})_{liquid} \xleftrightarrow{SPL} F^{-}{}_{(adsorbed)} \qquad (3)$$

$$(F^{-})_{liquid} \xleftrightarrow{SPL} F^{-}{}_{(precipitated)} \qquad (4)$$

Reaction (2) is expected to take place very rapidly. Dissolution of the white NaF salts was visually observed in pH 4 solutions. After addition of salts, in a few seconds, the solution cleared up showing that fluoride ions had been released very rapidly in solution. When amounts of salts added to water solution were above 75% of saturation concentration, dissolution was somewhat slower but remained inferior to a few minutes. The amount of fluoride used in the present study never reached this range.

Reaction 3 is an adsorption step, likely characterized by strong interactions between fluoride ions and spent potliner. This reaction can reach an equilibrium: further washing will result in the desorption of fluorides.

Reaction 4 is observed in the absence of mixing and is likely characterized by weak bonding between fluoride salts and spent potliner. These bonds are broken up easily by stirring.

As a result, the kinetics observed in the first part of this study are likely lumped kinetics from reaction 2 and 3.

The range of fluoride concentration obtained by leaching spent potliner, in this study corresponds to the results reported by numerous researchers including Personnet (1999) and Kimmerle et al. (1993) of fluoride concentration of about 5 g/L when spent potliner are leaching in concentration of a 100 g/L proving that adsorption is likely observed for all kind of spent potliner.

6.2.3.3 Fluoride adsorption modeling.

Using these data, two well known models can be used to describe the adsorption of fluorides: Freundlich and Langmuir.

The Langmuir model is defined by expression (1):

$$[F^-]_{adsorbed} = \frac{W_{\max} K[F^-]_{liquid}}{\left(1 + K[F^-]_{liquid}\right)} \qquad (1)$$

Where W_{max} represents the maximum loading of fluoride in g per g of spent potliner and K is a measure of the intensity of the adsorption isotherm (g/L). [Essington, (2004)].

Whereas Freundlich model is defined by expression (2):

$$[F^-]_{adsorbed} = K_F [F^-]^n \qquad (2)$$

Where K_F and n, represent adjustable parameters that are fitted to the experimental results, without physical meaning.

Table 6.2: adsorption Langmuir model parameters for various materials

Leaching solution	**Water**	**Na_2SO_4 Solution**	**Other Material**
W_{max} (g/g)	0.095	0.045	Spent potliner
K_c (L/g)	0.097	1.5	
W_{max} (g/g)	0.00049		Carbon
K_c (L/g)	180		
W_{max} (g/g)	0.018		Resin
K_c (L/g)	190		
W_{max} (g/g)	0.00842		α-Alumina
K_c (L/g)	1380		
W_{max} (g/g)	0.001204		γ-Alumina
K_c (L/g)	230		
W_{max} (g/g)	0.00628		Activated red mud
K_c (L/g)	162		
W_{max} (g/g)	0.00316		Original red mud
K_c (L/g)	34		
W_{max} (g/g)	0.00454		Hydroxyapatite
K_c (L/g)	2440		
W_{max} (g/g)	0.00179		Fluorspar
K_c (L/g)	91		
W_{max} (g/g)	0.0016		Activated Quartz
K_c (L/g)	86		
W_{max} (g/g)	0.00039		Calcite
K_c (L/g)	23		
W_{max} (g/g)	0.00019		Quartz
K_c (L/g)	12		

Langmuir model was favoured over Freundlich model, because the experimental results showed that adsorbed fluoride concentration reach a plateau (see figure 6.5). Spent potliner particles are approaching saturation above 50 g/L. Spent potliner will have to be washed at a lower concentration than 50 g/L if the amount of fluoride adsorbed is to be minimized. A Langmuir model of adsorption was fitted to the experimental results based on least square minimization methods utilizing Matlab (Nelder-Mead simplex). These results are compared to other studies involving fluoride adsorption (see table 6.2). The value found for W_{max} are in the right range, however, the value for K found in this study are about a thousand time lower than the ones reported in the literature. However, these studies reported involve the removal of fluoride from water to make it drinkable. The material selected for this type of study will strongly absorb fluoride at very low concentration. As a result, their intensity of adsorption ought to be very high and only material presenting this characteristic were studied. This is likely the reason why the value of K found in this study is significantly lower compared to other values found in the literature.

The predictions obtained with a Langmuir model fit reasonably well the experimental results (figures 6.5 and 6.6).

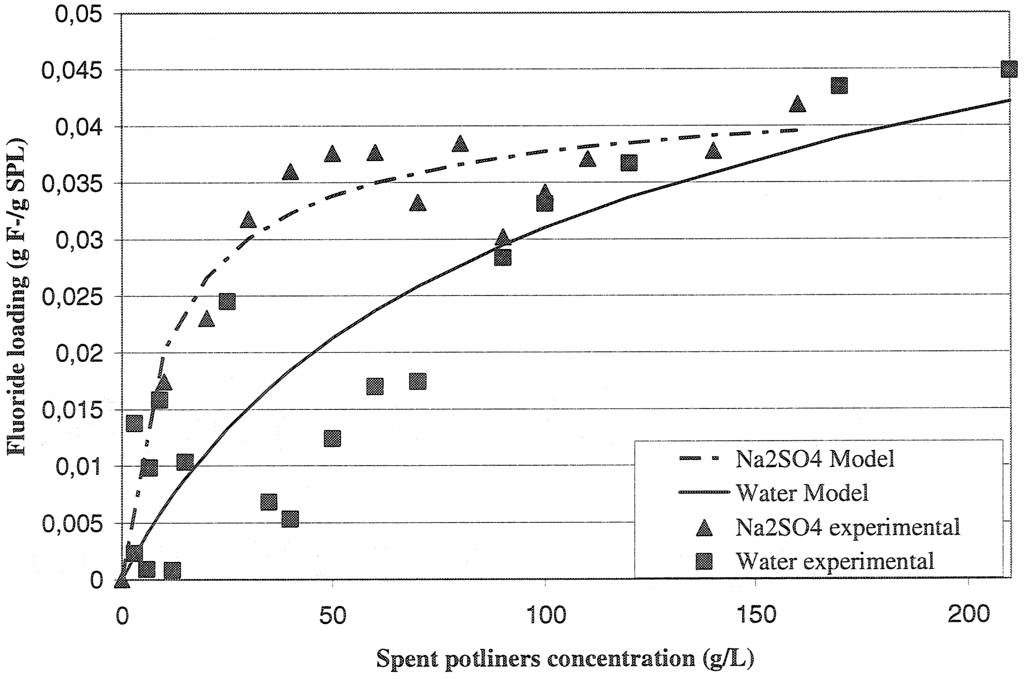


Figure 6.5: Predictions of fluoride loading per g of spent potliner particles at 25°C, pH=4.

However, the approach chosen is a lumped approach. All adsorption sites are considered equivalent. This is unlikely true, especially when the highly diversified composition of spent potliner is considered (refractory, cryolite, aluminium, iron, carbon etc…). A better adapted model could consist in taking account a distribution of adsorption reactions.

A second remark deals with the compared adsorption of fluoride when the leaching solution is either Na_2SO_4 or water. The data clearly show that fluoride ions are adsorbed more easily when high concentrations of salts such as Na_2SO_4 are present in the solution. It is likely related to the activation of some adsorption sites on spent potliner by sulphate ions.

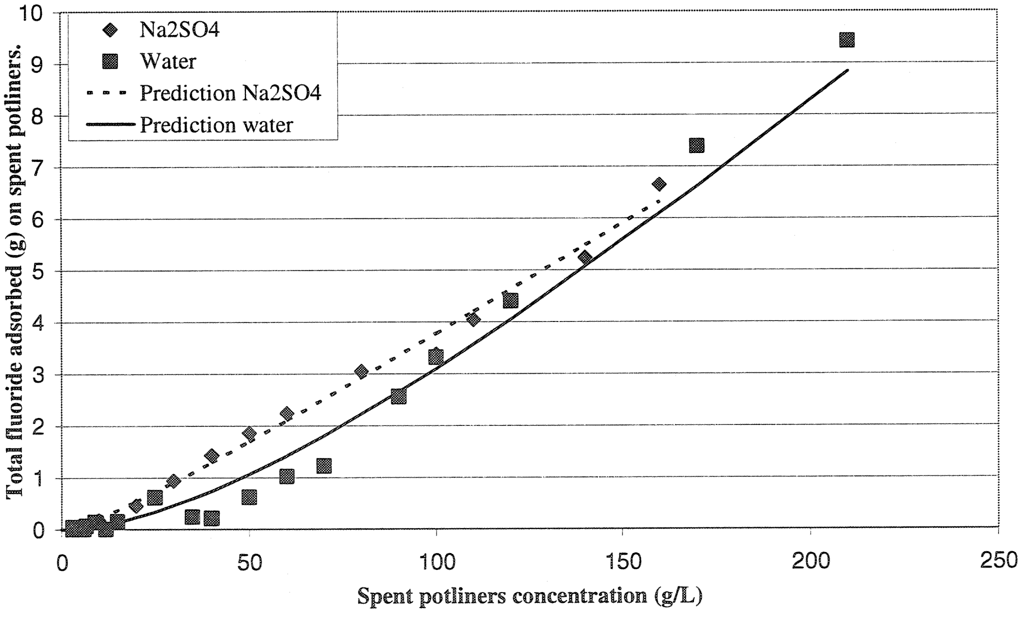


Figure 6.6: Total quantity of fluoride adsorbed on spent potliner particles and comparison with a Langmuir model.

The adsorption was found to be decreasing with increasing temperature (see figure 6.2). This result seems opposite to what is usually reported in the literature: it tends to indicate that the adsorption reaction is exothermic. However the experimental temperature range of other studies is narrower that the one used in this study. None of them have reported results above 45°C.

Finally, the pH of the leaching solution (see figure 6.7 and 6.8) is shown to have little effect on adsorption and kinetics of leaching. It could be related to the fact that many species present in spent potliner could adsorb: Carbon, cryolite, silica etc could all adsorb and present a maximum adsorption at different pH. The diversity of adsorbing species could explain why the pH does not affect adsorption. Consequently, the adsorption parameters found in this study will be applicable to a wide range of pH. Moreover, it is likely as well, that the reactions (2) and (3) are not affected by change of pH and are relatively independent of the composition of spent potliner and salts used in the leaching solution.

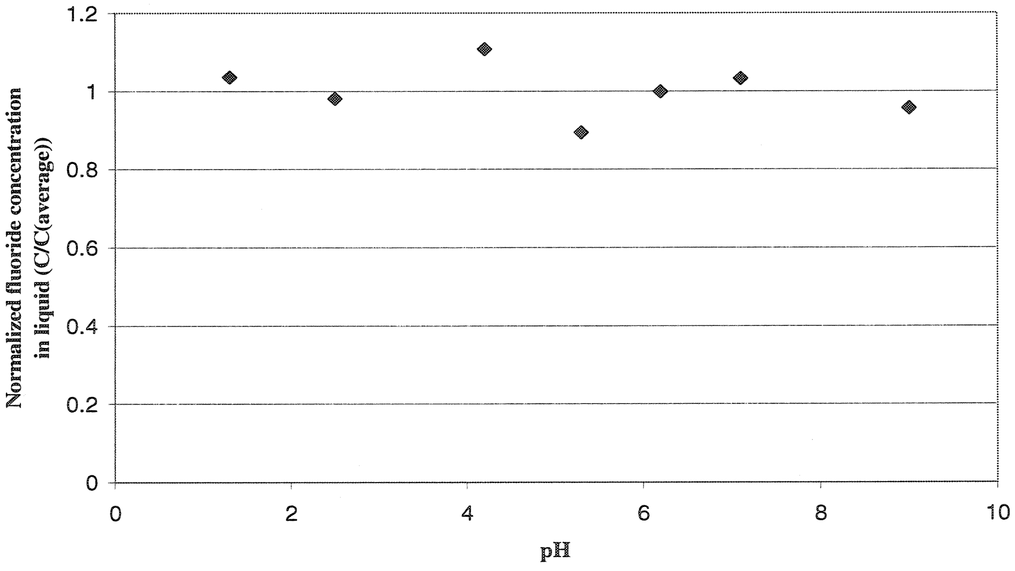


Figure 6.7: Effect of pH fluoride concentration in liquid, at SPL concentrations of 50 g/L, and temperature of 20°C.

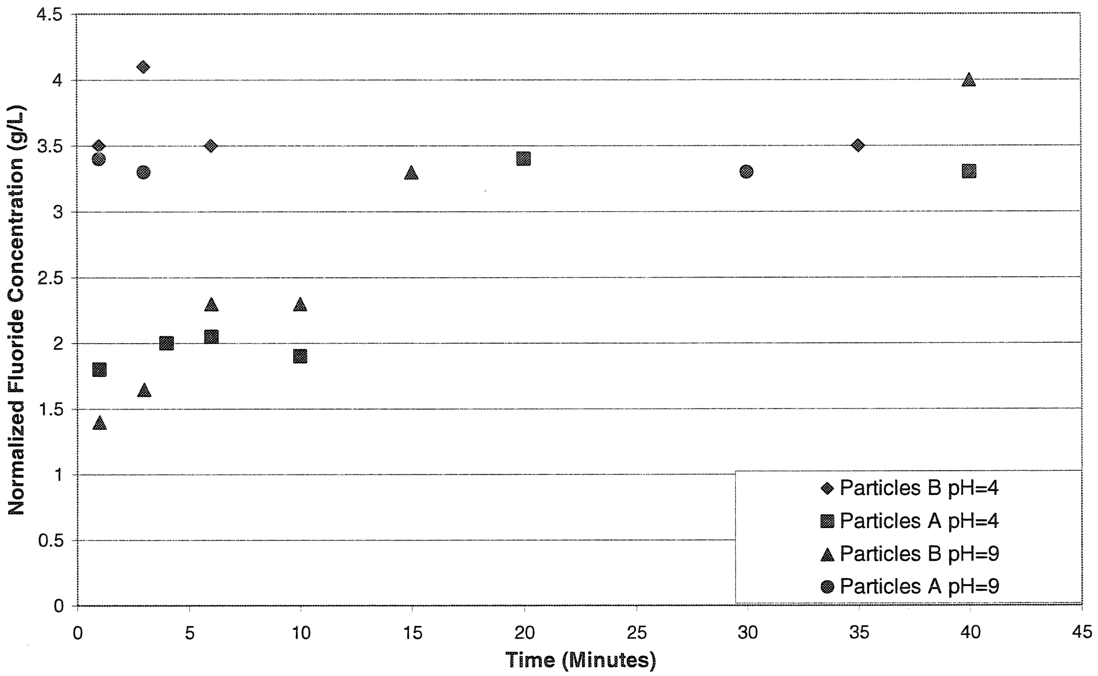


Figure 6.8: pH effect on leaching kinetics.

The results of this study can be used to estimate the quantity of water needed to treat spent potliner in a single step so as to wash fluoride leaching below an hypothetical 100 ppm measured by TCLP standards. Assuming perfect separation between liquid and solid phase after leaching, it is found that spent potliner should be washed in concentration of 20 g/L with water acidified by sulphuric acid. If the 50000 tons of spent potliner produced in Quebec alone are treated, it represents a minimum volume of water of 1000000 tons. This is the average yearly consumption of a 70000 inhabitant's city. This is an environmentally unacceptably high water consumption and the water ought to be reused in the process after elimination of fluoride.

However if the water is recycled, sodium and sulphate will concentrate in the solution. Sulphate salts will concentrate and lead to higher fluoride adsorption on spent potliner. Consequently, higher water to solid ratio will have to be used. Once a concentration of a

120 g/L Na_2SO_4 is reached, in order to comply with hypothetical 100 ppm regulations, solutions containing 8 g of spent potliner per liter of water should be used. Such a change in maximum concentration (20 g/L vs. 8 g/L) justifies why adsorption has been studied as well, when highly concentrated Na_2SO_4 solution are used.

6.2.4 Conclusion:

This study focused on the phenomenon of fluoride leaching from spent potliner. It was found that the mechanism of leaching is likely constituted of a two steps reaction involving the dissolution of NaF salts and adsorption of fluoride onto spent potliner particles. A third reaction is possible resulting in the precipitation of fluoride when spent potliner are let free to settle. Kinetics studies showed that a pseudo-equilibrium is reached immediately for small size particles. Experimental study of adsorption carried out either with pH 4 water or 120 g/L NaSO4 concentrated solution showed that an adsorption model based on Langmuir Isotherm was perfectly adapted to predict the levels of fluoride adsorption in both cases. The maximum loading of fluoride on the particles was found to be 0.095 g/L when water is used as a solvent and 0.045 g/L when a solution of 120g/L of sodium sulphate is used. These results were used to show that the water in a leaching process to clean up spent potliner of its fluoride content should be reused.

6.2.5 Acknowledgments:

We would like to thank Billy Servière for his help in the experimental part of this work, as well as Pascal Masciotra, and Pierre S. Turcotte for their financial support, and their expertise.

6.2.6 Reference:

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CHAPITRE VII :

DÉVELOPPEMENT ET VALIDATION D'UN PROCÉDÉ DE LIXIVIATION DES FLUORURES DES BRASQUES.

7.1 Présentation de l'article.

Ce dernier article est intitulé **'Development and validation of a leaching process of the spent potliners fluoride content'** soumis à la revue **Journal of Hazardous Material**. Cet article reprend les éléments de l'article précédent dont le mécanisme d'équilibre entre les fluorures et les brasques, ainsi que le modèle d'isotherme de Langmuir développé afin de décrire les données obtenues. Ce modèle est utilisé afin de définir un paramètre d'efficacité de lavage, qui caractérise la quantité de fluorure retirable des brasques en un lavage. A partir de ce modèle, un procédé complet de traitement des brasques a été bâti sur Aspen. Ce procédé implique :

- La lixivation des fluorures des brasques en trois étapes à contre-courant dans de l'eau acidifiée à l'acide sulfurique.
- La précipitation des fluorures par du calcium en CaF_2 insoluble.
- Le recyclage de l'eau de procédé ainsi que la précipitation des sulfates par addition de baryum.

Ce procédé a vu ensuite son fonctionnement optimisé en minimisant et les. coûts de production et les coûts d'investissements.

Le procédé optimisé a été validé par différentes expériences à certaines étapes clés afin de vérifier le fonctionnement du modèle.

7.2 Development and validation of a leaching process of the spent potliners fluoride content.

Référence: Yann Courbariaux, Jamal Chaouki*, Christophe Guy. (2004) :
'Development and validation of a leaching process of the spent potliner fluoride content.' Submitted to Journal of Hazardous Material.
Keywords: Spent potliner, fluoride, leaching, process modeling, Aspen, sorption.

7.2.1 Abstract:

In this study, the various processes developed to treat the fluoride content of spent potliner are reviewed and evaluated. A new hydrometallurgical process designed to reduce TCLP measured fluoride leaching of spent potliner to levels lower than 150 ppm is described. In this process, spent potliners are leached with a weak sulphuric acid solution and fluoride is then precipitated in CaF_2. The process water is recycled to minimize consumptions. The performance of this process configuration was investigated through the development of an "Aspen plus" simulation. In conclusion, good agreement was obtained between the experimental results and the predictions of the model. The process performance is satisfactory and respects Quebec fluoride leaching regulations. With additional leaching steps, more stringent regulations can be met. As well, Aspen can be used to adequately design fluoride leaching processes, and the new process developed could be adapted to any type of spent potliner in order to respect fluoride leaching environmental regulations.

7.2.2 Introduction:

Spent potliners are a byproduct of aluminium production. They originate from the removal of the carbon and refractory layer that constitutes the wall of reductions cells where dissolved bauxite is reduced to aluminum.

Spent potliner are considered an hazardous waste by the U.S. E.P.A. (Environmental Protection Agency) mainly because of its fluoride and cyanides content. Landfill is prohibited without prior suitable treatment. Their cyanide content can be eliminated by partial combustion (Courbariaux et al, 2004a).

A large diversity of processes has been developed to tackle the issue of spent potliner fluoride treatment. Fluoride salts constitute potentially a valuable resource for many processes:

- Steel making. Byers, (1986); Augood and Keiser, (1989)
- Cement production, Personnet , 1999.
- Cryolite synthesis. Fendel and Bings (1996).

The process developed can be classified in three categories:

1) Removal of fluoride by leaching followed by recycling or immobilization of fluorides (see table 7.1).

These processes are mainly aimed at recycling the various recoverable chemical elements contained in spent potliner (C, F, Na, Al). For most spent potliners, the main fluoride component of spent potliner is sodium fluoride which is relatively soluble in the proportion of 41.3 g per kg H_2O at 25°C. It is first artificially leached with water.

$$NaF + H_2O \rightarrow Na^+ + F^- \qquad (1)$$

The solubility of sodium fluoride is optimum in strongly acid solution because of the equilibrium HF/F$^-$.

Cryolite is the second component of importance and is considered to be non soluble in water but can be reacted with soda to yield soluble species.

$$Na_3AlF_6 + 4NaOH \rightarrow 6NaF + NaAlO_2 + 2H_2O \quad (2a)$$

Or it can be dissolved following the reaction with a strong acid (Pong et al., 2000).

$$Na_3AlF_6 + 3H_2SiF_6 \rightarrow 2AlF_3 + 3Na_2SiF_6 + 2HF \quad (2b)$$

It is expected that fluoride species other than NaF will not leach significantly in solution close to neutral pH.

Processes recovering the fluoride dissolved can either recycle it for cryolite production:

$$3NaF + AlF_3 \rightarrow Na_3AlF_6 \quad (3)$$

or permanently immobilize it as low solubility compound CaF_2.

$$Ca^{2+} + 2F^- \rightarrow CaF_2 \quad (4)$$

2) Permanent capture of fluoride in the form of CaF_2 salts at high temperature (600 to 800°C) (see table 7.2).

The following reactions are involved in this type of process: (Reynolds process)

$$2NaF + CaCO_3 + Al_2O_3 \rightarrow 2NaAlO_2 + CaF_2 + CO_2$$

$$2Na_3AlF_6 + 6CaCO_3 \rightarrow 3Na_2CO_3 + 6CaF_2 + Al_2O_3 + 3CO_2$$

(5a-5b)

or: (Split process)

$$2NaF + CaSO_4 \rightarrow CaF_2 + Na_2SO_4 \qquad (6)$$

This type of processes (table 7.2) requires the disposal and landfill of at least twice more residue than the amount of SPL treated. In addition, treatment at medium temperature implies having to tackle agglomeration risks (Brooks et al, 1992). Furthermore, the fluoride content of the SPL cannot be recycled, due to its low concentration in the residue obtained and little availability.

3) Permanent capture of fluoride through vitrification, (also called stabilisation or immobilization processes) and recycling of fluoride through the emissions of HF. (see tables 7.3)

These processes (Table 7.3a) involve the melting of spent potliner at high temperatures. Steam is blown off the melted mixture and reacts with fluoride to yield gaseous fluorhydrique acid. The HF produced is then collected and reacted with alumina to produce AlF_3.

$$NaF + H_2O \rightarrow NaOH + HF(g)$$
$$2NaF + Al_2O_3 + H_2O \rightarrow 2NaAlO_2 + 2HF(g) \qquad (7a\text{-}7b)$$

As a variation of the previously described processes, the removal of fluoride can be carried out at low temperature using high concentration of acidic solutions.

The main drawback of these processes lies in the recycling of fluorides through the emissions of gaseous HF, which is technically challenging. As well, the cost related to heating up the SPL to vitrification temperature is very high compared to other type of processes.

In conclusion, removal of fluoride by hydrometallurgical processes is the most popular option for their good overall performance (table 7.4). A large variety of processes have been developed and their feasibility studies have been reported in the literature. Advantages of this type of processes encompass:

- Low temperature operating conditions resulting in lower energy costs.
- Little agglomeration potential.
- Reduced corrosion conditions possible.
- Strong potential for the recycling of fluoride.
- Low toxicity of the end products obtained in case recycling is not profitable.

Table 7.1: Hydrometallurgical processes.

Name of process	Prior treatments	Fluoride treatment	Conditions (/ton of SPL)	Remarks
Alcan	Basic leaching	Forced precipitation of NaF by evaporation. Resolubilisation of NaF and precipitation of CaF_2 by reaction with $Ca(OH)_2$. Bayer liquor obtained (NaOH).	1.4 tons of water. 1.7 tons Bayer liquor obtained.	<65 ppm of Fluoride remaining in liquid.
Rethmann	Basic leaching at 80ºC with solution 2% NaOH.	NaF solution obtained and recycled in cryolite production by reaction with AlF3.	0.24 tons of cryolite recovered.	78 % fluoride recovered.
Comalco	Oxidation in Torbed without carbon combustion.	Basic leaching at 80ºC during 30 minutes and precipitation of CaF_2.	1.1-1.5 ton water needed 0.3-0.7 ton lime needed.	

Name of process	Prior treatments	Fluoride treatment	Conditions (/ton of SPL)	Remarks
Blayden	Batch water leaching	Fluoride in solution are precipitated using Ca(OH)2 and disposed of along with the SPL.	1.8 tons need to be disposed of.	$Ca(OH)_2$ is added with a 160 % excess to make sure all fluoride is precipitated.
Bush	Basic leaching with NaOH to dissolve NaF, followed by leaching with $H_2SO_4/Al_4(SO_4)_3$ solution to dissolve cryolite. Both solutions are used to obtain AlF_3.			Sodium and sulphates remaining in the solutions are used to regenerate sulphuric acid and soda.

Name of process	Prior treatments	Fluoride treatment	Conditions (/ton of SPL)	Remarks
Pong	Water leaching and dissolution of NaF which is recovered by precipitation with $CaCl_2$.	Acid leaching with HF to dissolve cryolite, precipitation of $NH_4(AlF_4)$ and production of AlF_3 by pyrolysis of precipitate.		
Deutschman	Oxidation in a rotative drum.	Water leaching followed by sulfuric acid leaching and precipitation of CaF_2 after addition of lime.		Co-precipitation of $CaSO_4$ observed.

Table 7.2: Mid-temperatures fluoride stabilisation processes.

Name of process	**Prior treatments**	**Fluoride treatment**	**Conditions**	**Remarks**
Reynolds	Oxidation in a rotative drum	Fixed in en CaF_2 during the combustion by reaction with $CaCO_3$.	1.4 tons filler needed. 2.4 tons of residues obtained.	Fluoride, Calcium and sicilium can react to yield cuspidine which can leach fluoride at basic pH.
SPLIT	Oxidation in a vortec reactor.	Fixed in CaF_2 during thermal treatment by reaction with calcium sulphate.	1 ton $CaSO_4$ needed	

Table 7.3a: Vitrification processes

Name of process	**Prior treatments**	**Fluoride treatment**	**Remarks**
Ormet [24]	Oxidation at very high temperature: 1200 to 1500°C.	Fluorides are either vitrified or collected at the smokestack as HF where it reacts with alumina to yield fluorspar.	Declared BDAT by the E.P.A. The residue can be potentially used to fabricate tiles
Ausmelt [25,26]	Oxidation in a molten slag bath	Fluorides are either vitrified (10%) or collected at the smokestack as HF where it reacts with alumina to yield fluorspar.	Most residues are marketable. HF is cleaned up by contacting it with liquid sulphuric acid.
Elkem [32]	Oxidation in a molten slag bath.	Fluorides are either vitrified or emitted after contact with steam as HF recycled in AlF3 production.	

Table 7.3b: Hydrometallurgical processes and recycling of fluorides through HF emissions.

Name of process	Fluoride treatment	Remarks
Gnyra [28]	Sulphuric acid is reacted with NaF, AlF_3 and CaF_2 in order to generate HF at 180-240°C. The HF generated can be reused to generate AlF_3.	97.9 % fluoride removal.

Table 7.4: Relative comparison of the various types of fluoride treatment in spent potliner (+++: very favourable, ++ favourable, + neutral, - negative).

	Temperature of process	Recycling options	Investments costs	Fluoride removal efficiency	Operating costs	Operating Difficulties
Hydrometallurgical processes	+++	+++ (High diversity of products possible)	+++	-	+++	+++
Low temperature Processes	+	- (Fluoride locked)	+	-	++	++ (agglomeration)
High temperature processes	-	+ (AlF_3 produced)	- (High temperatures equipment required)	+++ (Extremely low fluoride residual leaching)	+	+ (HF emissions)

However, leaching processes involve potential high costs, related to the large volume of reactors for the reaction to take place, long residence time, high quantity of additives needed to precipitate chemical species of economical interest and high purity required for the end product if recycling is an option. In order to minimize these costs, optimization is necessary, but in processes requiring many reactions steps, carrying out a full scale experimental optimization study is challenging. This is why it is common to resort to the development of models in order to predict the outcome of a process and facilitate its optimization.

7.2.3 Process description and its modeling.

The primary objective of the process developed is to remove the readily leachable fraction of spent potliner fluoride to allow its declassification as a hazardous waste. The second objective is to maximize recycling opportunites.

Neutralized SPL in contact with rain water or the buffer of TCLP tests will likely result in conditions in which leaching occurs at pH ranging from 4 to 7. After reviewing reactions (1) –(7), it is expected that these solutions are little susceptible to leach fluoride species other than NaF. Therefore the process will be designed to leach all the accessible NaF salts found in spent potliner and neutralize the naturally basic SPL. All other chemical species of fluoride will remain in the SPL. This can be achieved by resorting to weak acid leaching.

The design and modeling of a process requires a good knowledge of the reactions and kinetics involved. Unfortunately very little information is available in the literature on these subjects for spent potliner treatment. Consequently, an extensive study was carried out in order to verify the ability of Aspen to model the leaching of fluorides from spent potliner. Aspen (Advance System for Process Engineering) was selected for this work because of the large thermodynamics data banks available for common reactions. Aspen is widely used in the chemical process industry to model processes or to predict yields of reactors [Sotudegh et al, (1998); Yan and Zhang (1999); Horne et al. (1991)].

The model built could be used to optimize the leaching conditions of spent potliner depending on its initial composition.

In this, cyanide content of spent potliner will be supposed destroyed by either incineration or any other appropriate means (Courbariaux et al., 2004a). In the course of this study, the cyanide content of spent potliner was destroyed by incineration in an oven with reduced oxygen content at 700°C.

In order to build a full model using Aspen plus, the following aspects of the process have been validated experimentally:

1) Equilibrium is reached quickly after mixing of the reactants. Consequently, experimentally obtained batch reactions results and ASPEN continuous process predictions can be compared. (Courbariaux et al., 2004b)
2) The Aspen Swash unit model can be used to adequately model the leaching of fluorides. (see section stage 1: fluoride leaching)
3) Of all the fluoride species present in spent potliner, only NaF leaches. (See section 1 fluoride leaching).
4) Only the reactions presented in table 7.5 are considered. (Courbariaux et al., 2004b)

Table 7.5: Reactions considered in the ASPEN model

Number	**Reactions**
1	$2\ H_2O$ <-> H_3O^+ + OH^-
2	CO_2 + $2\ H_2O$ <-> H_3O^+ + HCO_3^-
3	HCO_3- + H_2O <-> H_3O^+ + CO_3^{2}-
4	H_2SO_4 + H_2O <-> H_3O^+ + HSO_4^-
5	HSO_4^-+ H_2O <-> H_3O^+ + SO_4^{2-}
6	HF + H_2O <-> H_3O^+ + F^-
7	HNO_3 + H_2O <-> H_3O^+ + NO_3^-
8	$BaOH^+$ <-> Ba^{2+} + OH^-
9	$CaOH^+$ <-> Ca^{2+} + OH^-
10	Na_2SO_4 <-> $2\ Na^+$ + SO_4^{2-}
11	$NaOH$ <-> Na^+ + OH^-
12	$BaCO_3$ <-> Ba^{2+} + CO_3^-
13	$BaSO_4$ <-> Ba^{2+} + SO_4^{2-}
14	$CaSO_4$ <-> Ca^{2+} + SO_4^{2-}
15	CaF_2<-> Ca^{2+} + $2\ F^-$
16	$CaOH^2$ <-> $CaOH^+$ + OH^-
17	Na_2CO_3 <-> $2\ Na^+$ + CO_3^{2-}
18	NaF <-> Na^+ + F^-
19	$NaHCO_3$ <-> Na^+ + HCO_3^-
20	$Ba(OH)_2$ <-> $Ba(OH)^+$ + OH^-
21	$CaCO_3$<-> Ca^{2+} + CO_3^{2-}

A detailed schematic of the ASPEN simulation flow sheet can be found in figure 7.1.

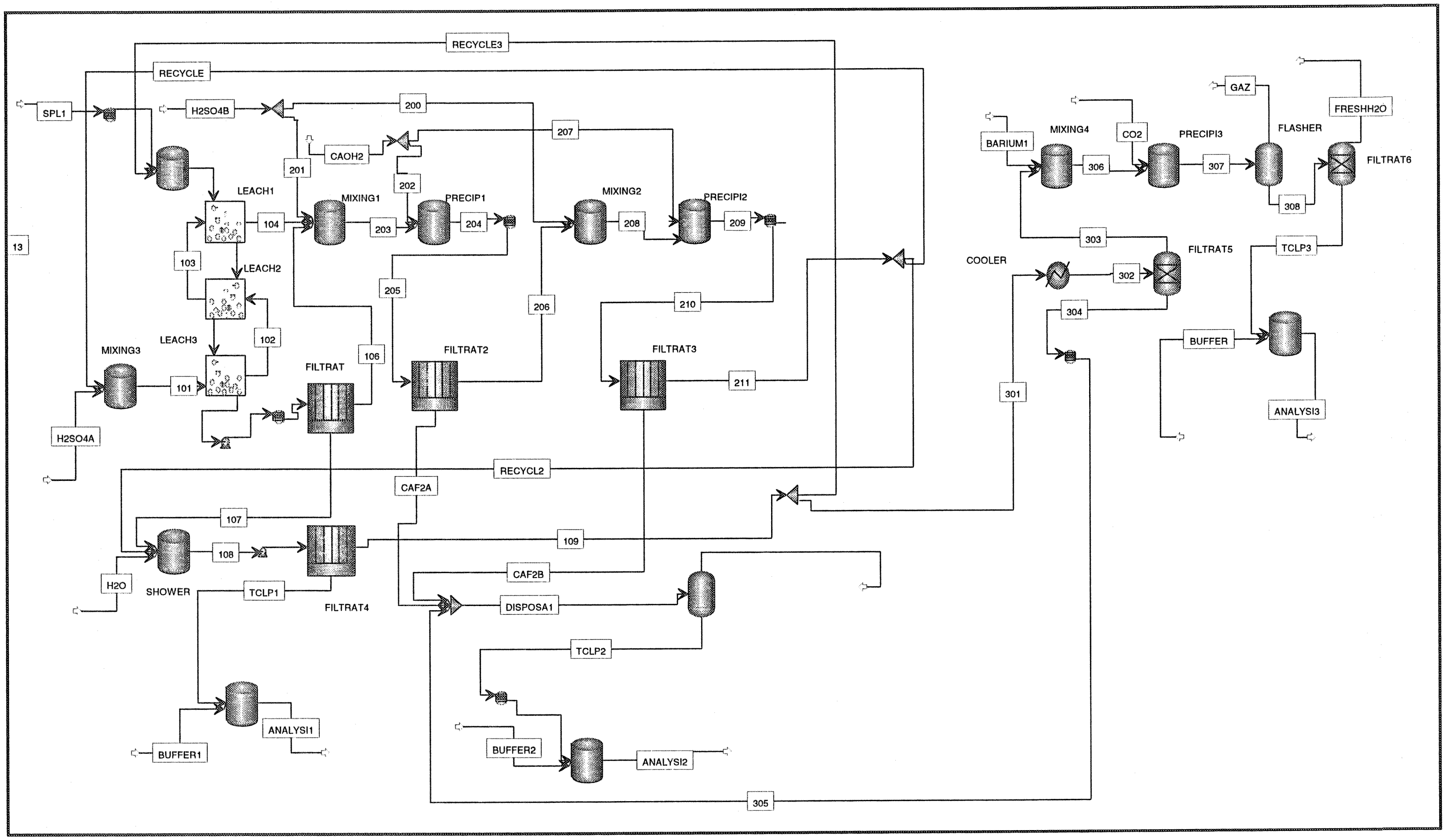

Figure 7.1: Schematic description of the treatment of spent potliner.
Numbers in 100's corresponds to the washing section of the process. SPL are showered and sent to TCLP analysis. Numbers in 200's corresponds to the precipitation of CaF_2. It is carried out in two steps: addition of $Ca(OH)_2$ and acidification with sulphuric acid. The liquid is then separated from the solids by filtration. Solids are sent off to TCLP analysis whereas the liquid is either recycled or sent to the water cleaning section of the process which corresponds to numbers in 300's. The liquid is first cooled down to 20°C, induced precipitate is disposed of. Barium oxide is added to the liquid, followed by acidification with CO_2. Precipitation, separation and TCLP analysis follows.

The process developed can be split into three different stages:

1) Fluoride leaching (100's)
2) Fluoride precipitation (200's)
3) Water treatment for recycling purposes (300's).

The numbers in 100, 200, 300's refer to the stages of the process described in the section below. The section related to 'TCLP' is not part of the industrial process but were used to help in obtaining predictions related to the process performance.

Stage 1: Fluoride leaching: Spent potliner are washed of their fluoride content, using the process recycled water in order to minimize water consumption. Spent potliner are then separated from the fluoride contaminated liquid by filtration.

The model simulations showed that in order to reduce water consumption, leaching of fluoride is better performed in three counter-current leaching tanks. High quantity of sulphuric acid (in the range of 0.6 tons of sulphuric acid per ton of SPL) is added to the process in order to maintain the pH of each tank between 3.5 and 5.5. Water recycled from other sections of the process can be used at this stage. Temperature levels are optimum around 25°C to keep energy consumption low and maintain high salts solubility. For each of the three leaching steps: solids are separated from the liquid by filtration and then directed toward a lower fluoride concentration tanks for further leaching. In the meantime, contaminated liquids are used to leach SPL containing more fluoride. After the three leaching in series, spent potliner are showered with low fluoride concentration recycled water and can be disposed of or recycled to other processes.

Stage 2: Fluoride precipitation: The fluoride content of the liquid is precipitated thanks to the addition of a calcium salt. Non-soluble salt CaF_2 is then obtained. Fluid and insoluble precipitate are separated by filtration.

Results of the model indicated that precipitation of fluoride is best carried out in two separate tanks in order to avoid the precipitation of other chemical species. Table 7.6 lists the other species susceptible to precipitate, along with their solubility characteristics. Even though calcium sulphate salts are highly soluble, because of the recirculation of water, sulphate concentrates in the liquid and will tend to easily precipitate once in contact with calcium. A two-step addition of calcium in precipitation tanks allow to reduce the amount of calcium added to each of them. Consequently, it limits the precipitation of calcium sulphate. The water exiting this stage of the process will present a very low fluoride content, less than 55 ppm. At this stage, 87.5% of the water treated is recycled to stage 1. Further recycling would results in undesired precipitation.

Stage 3: Recycling of water: The remaining fluid (12.5%) still contains heavy amounts of sodium ion and other dissolved salts. Most of the water is recycled to stage 1 while near to saturation levels. Extra-water is cleaned up.

Table 7.6: Solubility constants for common salts.

Precipitate	**Solubility (g/l)**
Barium sulphate $BaSO_4$	0.00243
Calcium sulphate $CaSO_4$	2
Barium oxide $Ba(OH)_2$	38.9
Barium carbonate $BaCO_3$	0.016
Calcium fluoride CaF_2	0.00025
Sodium fluoride NaF	41.3

Sulphate concentrated in recycle water can be removed by different ways. Four have been investigated:

1. Forced precipitation by addition of an organic solvent and recycle of the organic solvent by distillation.
2. Evaporation induced crystallisation to produce Na_2SO_4. (Kimmerle et al, 1993).
3. Electrochemical separation to produce H_2SO_4 and Soda. (Bush et al., 1986).
4. Precipitation of $BaSO_4$ by addition of $BaOH_2$.

After detailed cost and performance analyses were carried out, it was concluded that options 1) to 3) are either very difficult to carry out industrially or too costly with respect to the energy cost involved.

Consequently, Barium sulphate precipitation was favoured. It will be induced by the addition of $BaOH_2$ to the precipitation tank, which in conjunction with CO_2 acidification, leads to the release of Ba^{2+} ions and the precipitation of $BaSO_4$.

7.2.4 Experimental

The objectives of the experimental section of this study were first to test the validity of the assumptions taken and second to verify the predictions of the model for key-steps of the process.

7.2.4.1 Spent potliner used in this study.

The fluoride content of spent potliner was determined by using neutron activation analysis and was evaluated at 18.2 % by weight. The composition of spent potliner is highly variable. It is constituted of two fractions: carbonaceous and refractory fractions. Variations in the quantity of these fractions explain the variability of the samples and the variability of their leaching characteristics especially when small sample sizes are used for the experiments. In the course of this study, fluorides concentration in sample was found to range from 17.2 % up to 19.2%.

7.2.4.2 Stage 1: Fluoride leaching

7.2.4.2.1 Modeling of fluoride leaching.

Industrially, many different configuration of leaching reactors exist. In order to perform a mass balance around the unit and predict the fluoride content of the exiting liquid and solid streams, two parameters need to be evaluated:

- The water content of the solid stream at the exit of the unit
- The efficiency E of the leaching operation.

The water content of the solid stream is calculated by measuring the 'Liquid to solid mass ratio' parameters (LSrS). It represents the mass of the liquid plus dissolved solids in the liquid phase that is remaining with the solid fraction after separation of solid and liquid has been carried out. This ratio is set by the type of separator used. The best separation can be obtained industrially by filtering the solid.

Experimentally, the ratio was found by filtering various mixtures of spent potliner, water and sulphuric acid, and then measuring the amount of water remaining with the solid sample by evaporation. The density of the separated liquid phase was then measured and the density of the separated liquid phase was assumed to be similar to the composition of the liquid within the solid pores. These results were used to evaluate the LSrS which varied between 0.75 (fresh water) and 1 (recycled solution) depending on the liquid used to wash the solids.

The efficiency of leaching E is defined as (Treybal, 1987):

$$E = \frac{X_0 - X_{out}^L}{X_0 - X_{out}^S} \qquad (1)$$

Where, $X_0, X_{out}^L, X_{out}^S$ represents respectively the fraction of dissolved salts in: the inlet stream, in the liquid phase of the outlet liquid stream and in the entrained liquid phase of the solid outlet stream.

In models using this type of efficiency, three phases are considered: the liquid phase exiting the reactor (free of solids), the solid phase, with the remaining solid being inert, and the liquid phase contained in the solid stream that contains all unreacted remaining salts in spite of the fact that they may not be dissolved yet. Consequently, the efficiency of the leaching operating is optimum when the liquid phase and the solid phase liquid fraction have the same composition.

The ASPEN modeling unit selected to represent this type of industrial unit is the 'SWASH' unit or solid wash unit.

The efficiency of the leaching operation is very variable. When very high, a leaching process is then called a 'wash'. It can be affected by the following factors [Lott et al., (1972); Tomiak, (1984);Boydell et al, (1979); Farrow et al. (2000), Lu et al., (1992)]

1. Mixing limitations: the dissolved salts are caught in the liquid phase surrounding the particles which is not mixed with the rest of the liquid.
2. Non-ideality of the reactor. In this type of problem, the reactor presents dead zone and bypass of the liquid or solids which prevents an efficient mixing. (Venter et al., 1999)
3. Slow kinetics, which prevents the release of the salts in the liquid phase within the duration of the leaching steps.
4. Secondary reactions related mainly to the sorption of fluorides on the surface of the particles.

Limitations 1 and 2 can be reduced to a minimum by choosing an appropriate design for the leaching tanks. It has been shown that the leaching reaction was unlikely to be limited by mixing or bypass related problems because of the small particle size. (Courbariaux et al., 2004b). As well, the same experiments have shown that the kinetics of reaction are extremely fast and that equilibrium or pseudo-equilibrium can be reached in a few minutes. Consequently, only limitation 4 remains an issue. Adsorption of fluoride has been extensively experimentally studied in the literature on material such as biological material, mineral oxides, activates carbons, polymer resin, fly ash etc. [Sinha et al, 2003; Cengeloglu et al. (2002); Fan et al (2003), Lay et al., (1996); Bharagava et al, (1992); Leyva Ramos (1999)].

For fluoride adsorption on spent potliner it was found that leaching of spent potliner likely follows this scheme (Courbariaux et al, 2004b),:

NaF salts are rapidely dissolved.

$$(NaF)_{SPL} \rightarrow Na^{+} + F^{-} \tag{8}$$

Fluoride in solution adsorbs strongly and the adsorption is likely activated by sulphate ions.

$$(F^{-})_{liquid} \xleftrightarrow{SPL} F^{-}{}_{(adsorbed)} \tag{9}$$

Free fluoride in solution, in the absence of agitation can precipitate.

$$(F^{-})_{liquid} \xleftrightarrow{SPL} F^{-}{}_{(precipitated)} \tag{10}$$

Adsorption was modeled using a Langmuir isotherm with the parameters recorded in table 7.7.

Table 7.7: Langmuir model parameters for fluoride adsorption.

Leaching solution	Water	Na_2SO_4 Solution
W_{max} (g/g)	0.095	0.045
K_c (L/g)	0.097	1.5

7.2.4.2.2 Experimental validation

The first step of modelling of fluoride leaching processes was to verify if Aspen could predict adequately fluoride concentration when a reaction has reached equilibrium. In order to do so, 45 gr of pure NaF was dissolved in two 1-liter solution acidified to pH 4 by using sulphuric Acid. The first solution was constituted of pure water, whereas the second one had 120 mg of Na_2SO_4 dissolved in it. The objective was to verify if Aspen could correctly predict the interactions of ionic species in high concentrations and so take into account the ionic strength of the solution. The advantages of such set up were double: solids were almost completely dissolved and as such did not have any detrimental effects on mixing in the reactor, and separation of liquids and solids was not necessary. Consequently, its behaviour can be considered ideal. In the pure water case a concentration of fluoride of 18.4 g/L was found against a calculated value of 18.6 g/L, whereas in the case of the Na_2SO_4 solution, a concentration of 16.6 g/L was found against a calculated value of 16.1 g/L. The difference between experimental and calculated value are negligible, as a result ASPEN can be used to predict the dissolution of NaF salts in an ideal reactor setting.

With the Langmuir model developed, it is possible to predict the efficiency of leaching, such as defined by equation (1). Matlab was used to build an algorithm solving the Langmuir equation and predicting the concentration of fluoride in liquid and adsorbed on solid depending on the initial concentration of fluoride leachable and the mass of particles in the liquid. These results were then used to calculate the leaching efficiency. Figure 7.2 and 7.3 illustrates the results obtained in two situations for both leaching media:

- The amount of spent potliner is varied in solution, but about the amount of leachable fluoride per g of spent potliner is constant at 10% of the initial weight of spent potliner. These results are important to decide the ratio of washing liquid to spent potliner in the leaching process.

- The amount of spent potliner is fixed at 50 g/L but the amount of leachable fluoride is varying. These results will be useful in the final leaching stage, once spent potliner leach very little.

The adsorption of fluoride increases as more spent potliner is found in the solution and NaF dissolves. However fluoride adsorption reaches a maximum for solutions containing about 50 g/L of spent potliner (Courbariaux et al, 2004b). Consequently, the concentration of 50 g/L was chosen as the reference for the process.

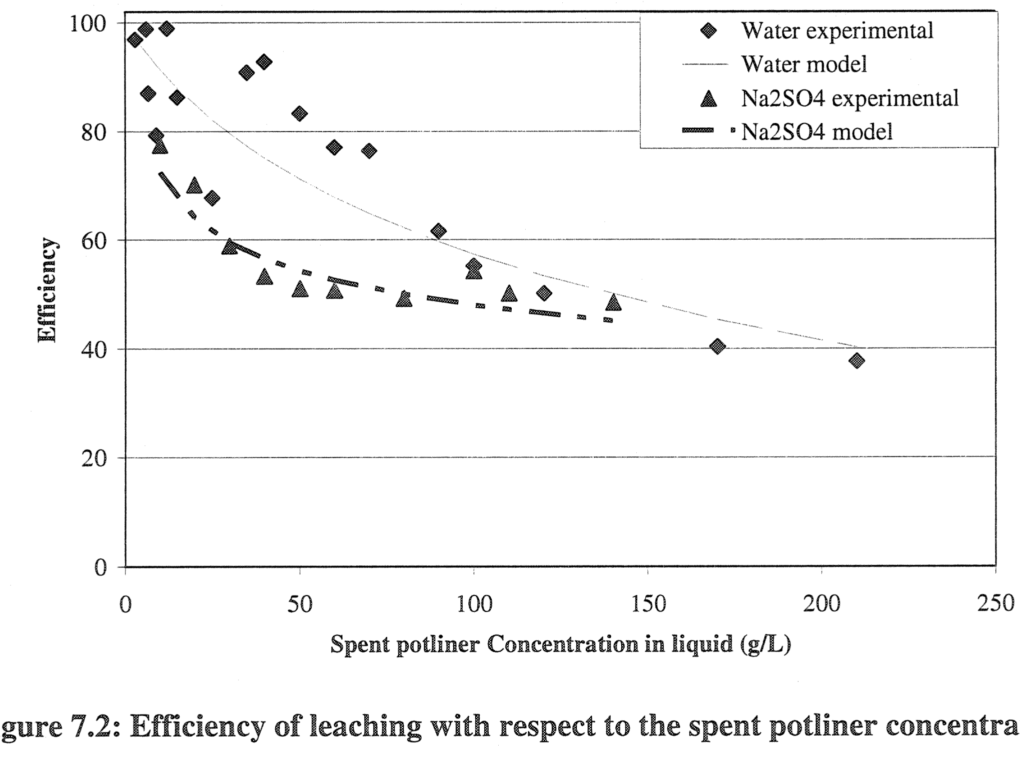

Figure 7.2: Efficiency of leaching with respect to the spent potliner concentration and considering that 10% of the initial weight of spent potliner is leachable fluoride.

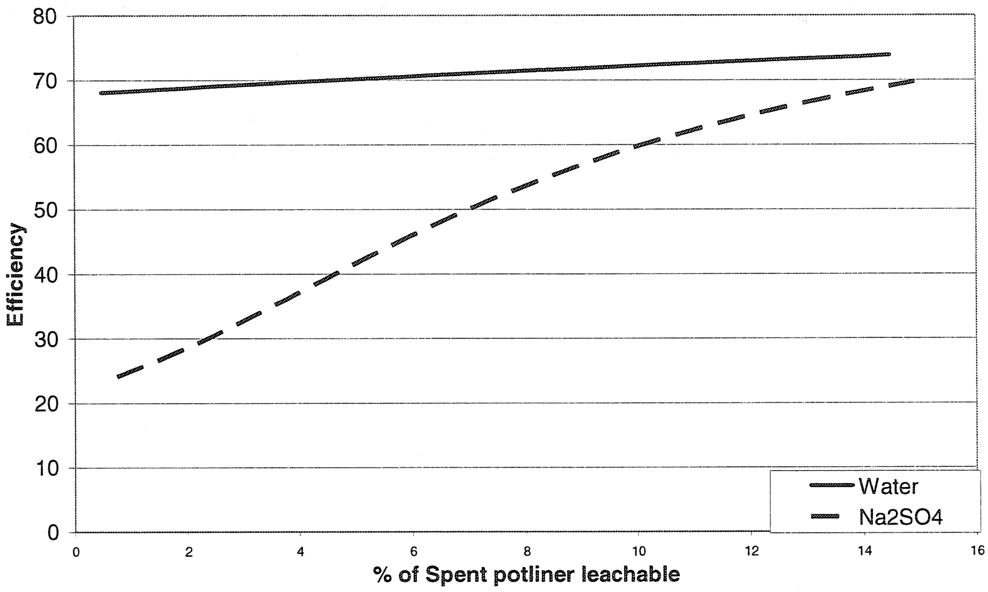

Figure 7.3: Efficiency of leaching with respect to the percentage of the initial weight of spent potliner that is leachable fluoride and considering that the initial weight of spent potliner is constant at 50 g/L.

One figure 7.3, the efficiency of Na_2SO_4 wash is much lower than water washes; this is due to the higher adsorption level at low concentration of spent potliner in the presence of Na_2SO_4 salts. These results are very useful in the final leaching stage, when spent potliner leach very little.

In order to fully verify the predictions of the Aspen model, it was used to predict the compositions of fluoride concentrations in three process simulations:

- Case 1: Water leach at a concentration of 50 g/L of spent potliner and a pH varying from 3.5 to 5.5 depending on the leaching step, and a temperature of 25°C. The conditions were found by not recycling any water in the process described in figure 7.1.

- Case 2: Recycled water leach, at a concentration of 50 g/L spent potliner and with solutions contained about 120 g/L of Na_2SO_4 at pH varying between 3.5 to 5.5 depending on the leaching step, and a temperature of 25°C. 87.5% of the water used in the process is recycled.
- Case 3: Water leach at a concentration of a 100 g/L of spent potliner and a pH varying from 3.5 to 5.5 depending on the leaching step, and a temperature of 25°C. The conditions were found by not recycling any water in the process in figure 7.1.

Case 1 and Case 3 do not represent an optimal process since fresh water is used instead of recycled water. However these two cases are studied for the sake of verifying the leaching model.

Case 2 simulation involves the recycling of process water and is the most similar to the process being proposed. However in stage 2 of the process, fluoride concentrations drops to very low level (55 ppm). The water recycled will then contain very low amount of fluorides and significant amount of calcium. This calcium, in the process is then put into contact with fresh spent potliner and will affect the leaching characteristics of fluoride. The Langmuir model has not been developed in conditions in which fluoride could be precipitated by calcium. Moreover, as explained in the upcoming section concerning TCLP results, Langmuir model can not be used to predict very low levels of fluoride leaching (below 100 ppm). Consequently, in order to validate the leaching model used, it was decided to use lower the amounts of calcium added in the process till lowering it further would not have an effect on fluoride concentrations in the leaching steps (about 5% less than optimum). These were the conditions used to test the leaching model.

The compositions of all the streams for the full process of spent potliner treatment, including the recycling loops was obtained by ASPEN. The efficiency of the washing steps was found by set by trial and error method, till the efficiency used for each wash step corresponded to the one calculated in these conditions by MATLAB. Figure 7.4 illustrates the algorithm used to converge towards an appropriate process.

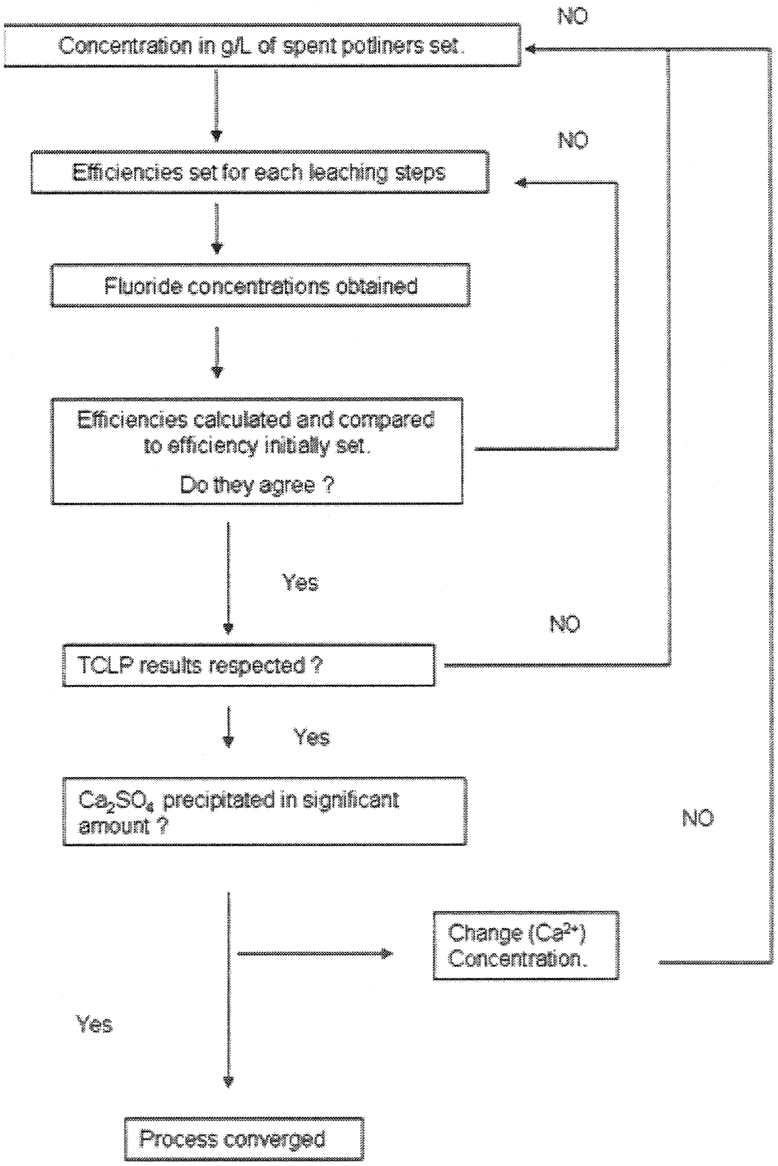

Figure 7.4: Decision algorithm in order to converge towards a satisfactory solution for the leaching process.

As a result, the compositions of the three leaching solutions were obtained. With this composition, three artificial solutions representing the composition of the leaching tanks were made for the three cases. An experiment was performed to test the predictions of the model for three washes in a row, with solutions approaching the conditions reached with recycled water at steady state.

The results of these simulations for each step can be seen compared to predictions on figure 7.5. The average error for the first step is 7%, the second step 22 % and the third step is 29 %. The error margin keeps increasing as the predictions of the third step used data incoming from the second step which depends itself from data incoming from the first step. As a result, the errors keep adding up justifying the 29% deviations observed for the third step.

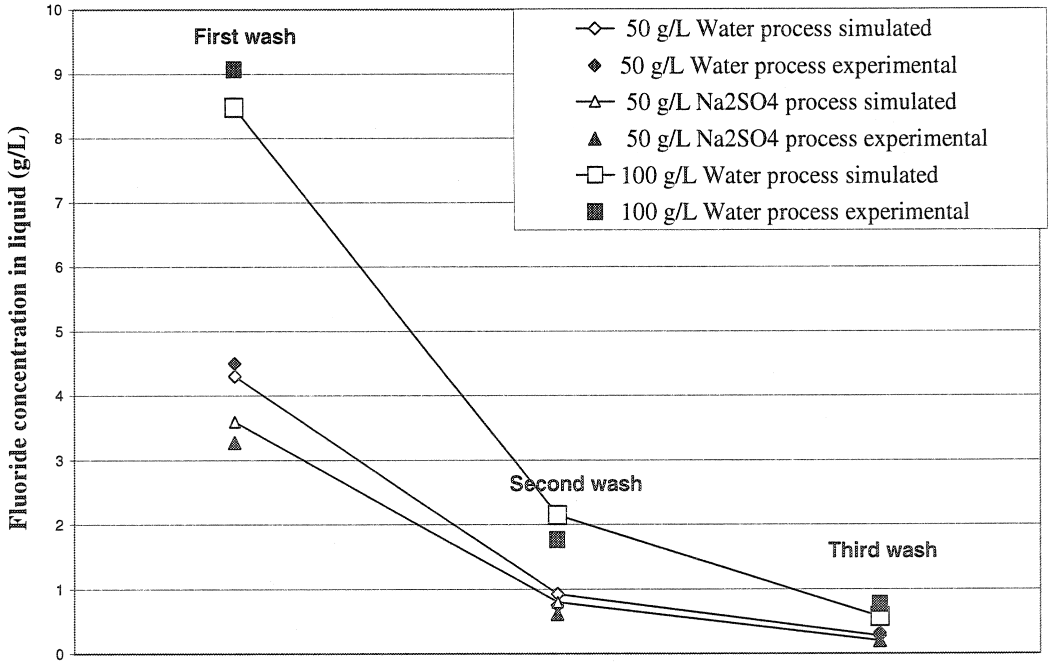

Figure 7.5: Comparison between model results and experimental result in various process configurations.

The samples obtained for each case were then showered using fresh water at a ratio of about 1:3. The slightly contaminated water used is then reused in the first washing of fresh spent potliner as a source of fresh water. The objective of this shower is to remove the layer of water surrounding the particles and having the fluoride content of wash 3 and increase the pH of the residue closer to neutral. The showering was carried out in the buchner filter and was completed in a few seconds. The modeling of the showering process is very difficult. Predictions were obtained by simply considering that only the water remaining with the solid was replaced and that the showering water did not remove any adsorbed fluoride. By doing so, fluoride desorption is neglected and the fluoride content of the particles is over evaluated.

7.2.4.2.3 TCLP tests of residues.

The leaching characteristics of the residues obtained were evaluated using the US TCLP procedure. This procedure is very similar to the procedure used in Québec except for the residence time of 24 hours instead of 18 hours. The regulations in Québec imposes concentrations lower than 150 ppm. Experimentally, two types of TCLP were carried out; the first one involved a buffer at pH 4 and the second one distilled water.

Predictions of the results obtained by TCLP were made by calculating the fluoride concentration in the solution in equilibrium with absorbed fluoride. Table 7.8 compares the results obtained. TCLP measurements with the buffer solutions are always higher than the one obtained by using distilled water. This is likely due to secondary reactions taking place at lower pH. The results obtained agree with the one obtained by the model and respect the Quebec regulations.

However, if more stringent regulations need to be met, further washing would not be enough. Indeed, experimental performed extra washes did not significantly decrease the results obtained by the TCLP which still hovered around 80 to 130 ppm. This phenomenon was observed as well by Blayden et al., 1987) and Deutschman (1987) who reported noticing a residual leaching concentration of about a 100 ppm that could not be reduced by washing. Adrien et al. (1996) report encountering difficulties with residual fluorides leaching related to cryolite. The residual leachable fluoride concentration found in this study is possibly related to cryolite dissolution, even though it is reported to be insoluble (handbook of physics and chemistry).

In order to verify if cryolite is likely responsible for residual leaching, XRD measurements were performed on various samples of spent potliner: initial calcined sample, after the first wash and second wash, and following an extra basic wash. Figures 7.6 and 7.7 present the results obtained with the arrow indicating were NaF and cryolite peaks are located. As can been from these measurements, NaF concentration decreases sharply after the first wash, whereas the cryolite peak is reinforced after each wash likely due to its concentration in the remaining solid resulting from the washing of all other species. The presence of cuspidine was not detected.

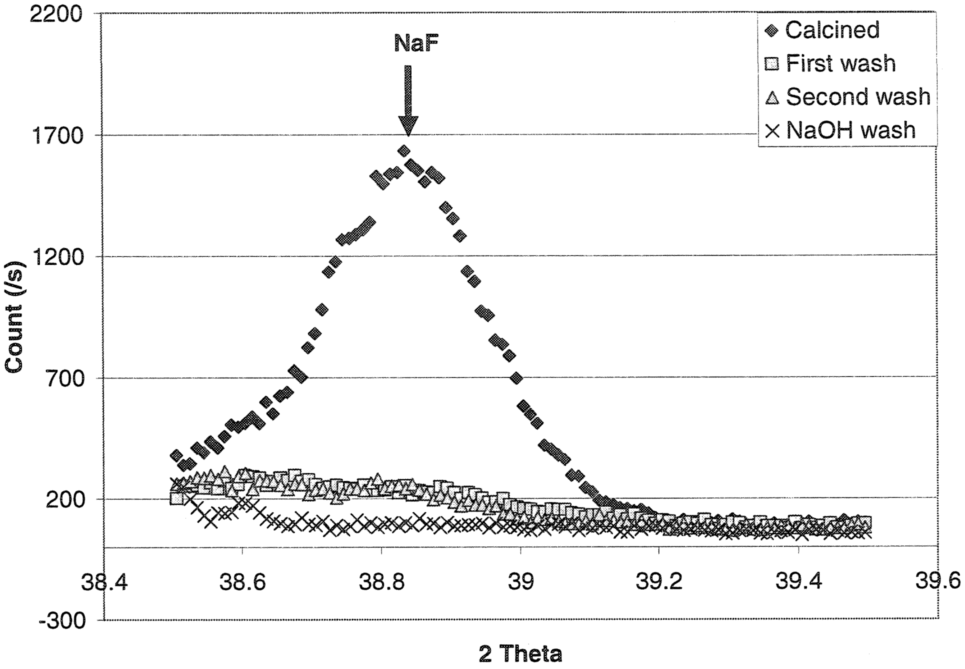

Figure 7.6: XRD measurements aimed at revealing the presence of NaF.

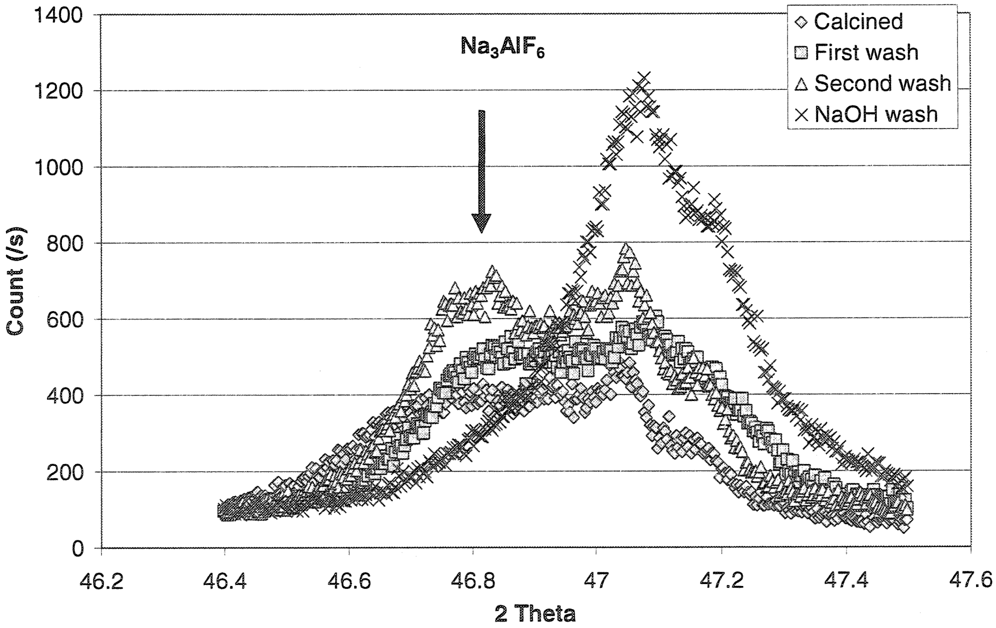

Figure 7.7: XRD measurements aimed at revealing the presence of cryolite Na_3AlF_6

The residual fluoride concentrations become leachable at very high basic or acidic conditions (Personnet, 1999). Two additional washes carried out at first at low pH (pH=1) and then high pH (pH=10.5) lowered the residual leaching of fluoride to 30 ppm. As can be seen with XRD measurements, on figure 7.7, the harsh treatment likely resulted in the removal of cryolite and the decrease of the fluoride residual leaching. The lack of thermodynamics data concerning the reactivity of either cryolite prevents the modeling of this section of the process. It is not possible to lower the TCLP measurements to values lower than 25 ppm, since it corresponds to the solubility of CaF_2.

In order to further verify the assumption related to the slow dissolution of cryolite, synthetic cryolite was purchased, thoroughly washed to remove impurities and was submitted to a TCLP leach test. The residual concentration of fluoride in the liquid was a 106 ppm, which is a value in the range expected.

Table 7.8: TCLP measurements on residue from leaching process.

	TCLP Predictions	TCLP Buffer	TCLP Distilled water
Water leach 50 g/L	83 ppm	118 ppm	93 ppm
Na_2SO_4 leach 50g/L	92 ppm	137 ppm	102 ppm
Water leach 100 g/L	262 ppm	305 ppm	170 ppm

7.2.4.2.4 Optimum model.

Case 2 modeling did not represent the optimal conditions of the process: 5% less calcium was added to the fluoride precipitation stage. If the optimal conditions are used along with the same model for efficiency predictions, and with sufficient addition of calcium to lower fluoride concentration in recycled water to 55 ppm, then, only the fluoride concentrations predicted in the liquid phase of leaching steps 2 and 3 of the process are inaccurate:

- 4 times lower fluoride concentrations in liquid phase of leaching step 3 at 49 ppm instead of 200 ppm. Such low concentrations are impossible, since fluoride concentration cannot drop below 100 ppm because of cryolite.
- 1.5 times lower fluoride concentrations in liquid phase of leaching step 2 at 520 ppm instead of 800 ppm.
- 1.06 times lower fluoride concentration in liquid phase of leaching step 3 at 3.3 g/L instead of 3.57 g/L.

This is why the leaching model could not be validated in such conditions, since two concentrations out of three would not have been strongly affected by calcium concentration. Leaching step 3 is little affected, because of its high fluoride concentration.

Moreover, the experimental results showed that with 5% less calcium added (non optimal conditions), fluoride leaching properties of residues already verified fluoride regulations. Consequently, with more calcium added, fluoride concentrations will be even lower, and fluoride regulations will be respected anyway.

7.2.4.3 Stage 2: Fluoride precipitation:

7.2.4.3.1 Analysis

In this stage the main objective is to recover fluorides from the liquid as a precipitate. This is realized by adding calcium carbonate to the solution and precipitating calcium fluoride. Calcium fluoride is a little soluble salt that is recovered by filtration. The solid recovered by filtration can either be landfilled or recycled. In the case landfill is the objective, the residue should not leach any species damageable for the environment. In the recycling case, its purity should be high in order to constitute a raw source of fluoride of high quality.

In both cases, mixing of precipitates with a soluble species should be avoided.

In order to precipitate CaF_2, Ca^{2+} must be introduced in the reactor. This can be done by adding either $CaCO_3$ or CaO or $Ca(OH)_2$.

$$CaCO_3 + H_2O \rightarrow Ca^{2+} + CO_3^{2-} \rightarrow Ca^{2+} + CO_2 + 2OH^- \tag{6a}$$

$$CaO + H_2O \rightarrow Ca^{2+} + 2OH^- \tag{6b}$$

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^- \tag{6c}$$

$CaCO_3$ is more difficult to use due to the release of CO_2. The least expensive to use is CaO obtained directly from the calcinations of lime. However $Ca(OH)_2$ was ultimately selected due to its ease of use.

In the following section, the process investigated corresponds to the optimum process and the quantity of calcium added (about 60 kg of calcium per ton of spent potliner) has not been lowered. The efficiencies used in the leaching section of the optimum process were not modified since for this step of the process, the important parameter is the fluoride concentration of the final leaching solution which is not significantly affected by the decrease of the quantity of calcium added.

7.2.4.3.2 Model evaluation

CaF_2 precipitation was observed visually to be immediate. Low concentration fluoride solutions clouds immediately after addition of stoecchiometric amount of Ca^{2+}. The clouds thickness does not increase further after the reaction has taken place.

Precipitation experiments were carried out and three key-parameters were evaluated in order to allow and adequate testing of the model predictions to the experimental results.

a) Fluoride concentration of the end solution,

The experiments were carried out by using a solution obtained after leaching of 50 g/L of spent potliner with solutions concentrated at 120 g/L of Na_2SO_4.The experimentally measured concentration range was 30 to 40 ppm. The model predicted a fluoride concentration in the range 55 ppm showing a good agreement with the experimental results.

b) $CaSO_4$ composition of the solid precipitate,

In order to limit impurity precipitation, the quantity of calcium added to the reactor needs to be minimized and so must be adapted to the fluoride concentration of the liquid that needs to be treated (Deutschman, 1987). As a result, with this objective in mind, accurate evaluations of the fluoride concentration in the liquid to be treated are essential. If the fluoride concentration is overvalued then the non reacted Ca^{2+} will precipitate as $CaSO_4$. In order to limit this risks a two steps fluoride precipitation configuration was used in the process developed. As a result only the precipitate of the second reactor will contain possible precipitate of $CaSO_4$.

The model predicted that the precipitate obtained would contain about 4 % $CaSO_4$. The experimental measurements showed $CaSO_4$ concentrations at 2.55%, 4.60%, 5.10% and 12.5 %. Except for the least experiment is not considered, the $CaSO_4$ predictions agree with the experimental results.

c) TCLP of the residue obtained,

The CaF_2 residue obtained were submitted to a TCLP test showing that they leach about 15 ppm of fluoride. The model predicted fluoride leaching level to be at 24 ppm.

In conclusion, the quality of the prediction in the precipitation stage of the process illustrates the accuracy of the model for well-known reactions. This is further demonstrated in the treatment of the sulphated water by barium oxide.

7.2.4.4 Stage 3: Treatment of water:

The water treatment required will vary depending on the location of the plant. Many countries do not consider restrictions on the release in city sewage system of highly concentrated Na_2SO_4 solutions. However, in case it would be necessary, the treatment of water using $Ba(OH)_2$ has been modeled and tested in non-optimum conditions. Experimental results showed concentrations in the vicinity of 3-4 ppm for remaining sulphate, whereas it was predicted that the concentrations would be 3 ppm. The water obtained could possibly reused as a source of fresh water for the rest of the process.

7.2.5 Conclusion:

Over the past thirty years, numerous spent potliner fluoride treatment processes have been developed. The literature review has shown that hydrometallurgical processes are preferred by most. However spent potliner is a very variable waste and the conditions of treatment adapted to one type of SPL will not be optimal for another type of SPL. With a model predicting the performance of a particular process, optimization can be performed and processes adapted without having to resort to time consuming and lengthy laboratory testings.

Experimental results showed that ASPEN could be used to model fluoride leaching of spent potliner and that the process developed could be used to treat the fluoride content of spent potliner. The treated residues obtained leach less than 150 ppm. However more work is needed to identify low solubility fluoride compound behaviour in spent potliner in order to model their dissolution in high pH conditions and lower residual leaching to less to 30 ppm.5.7

7.2.6 Acknowledgments:

The authors would like to thank P. Masciotra and P. Turcotte for their help in the development of the process, their expertise and their useful advice.

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CHAPITRE VII :

DISCUSSION GÉNÉRALE

La revue de littérature a souligné l'importance de la problématique de la génération de brasques. De nombreux projets de procédés de traitement ont été mis au point avec des résultats mitigés souvent du fait du manque de flexibilité des procédés ainsi que d'hypothèses de recyclage de sous-produits infondées. Un fort besoin existe de développer un procédé qui soit simple, flexible, universel et dont la minimisation des coûts ne dépende pas du recyclage de sous-produits. De plus il est nécessaire de procéder à une étude plus scientifique de la problématique des brasques afin de permettre de régler cet épineux problème dans les années à venir.

Au cours de ce travail, l'approche retenue a été de séparer le traitement des cyanures de celui des fluorures. L'objectif étant ainsi de pouvoir procéder à une optimisation des traitements de manière séparée, ce qui favorise la flexibilité du procédé.

Suite à une revue de la littérature exhaustive, la solution technologique retenue implique que les cyanures doivent être détruits par incinération à des températures légèrement inférieures au point d'agglomération des brasques (800°C). Cette approche permet d'augmenter l'efficacité de traitement par rapport aux techniques de lixiviation, et présente des coûts et difficultés techniques moins importantes que dans le cadre de la vitrification des brasques. Cependant cette technique nécessite l'utilisation d'additifs agglomérants tels que des particules de petites tailles qui vont se coller sur les particules de brasques afin d'empêcher leur agglomération. La cinétique de réaction obtenue, permet une optimisation des procédés d'incinération et démontre que des temps de résidence très faible à hautes températures sont suffisants pour détruire de façon efficace les cyanures.

Ce travail est conjugué à l'obtention d'une cinétique décrivant la combustion du contenu carboné des brasques. Le modèle obtenu est très robuste, novateur et précis, et permet de prédire avec efficacité la conversion du carbone lors de la combustion des brasques. Les brasques brûlent beaucoup plus lentement que les cyanures ne sont détruits, ce qui permet de contrôler l'augmentation de la température lors de l'incinération.

Dans une deuxième partie, la problématique de la gestion des fluorures est abordée. Une étude complète du mécanisme de lixiviation des fluorures démontre que ces derniers sont facilement lixiviables, mais adsorbent fortement sur les brasques. Par conséquent un nettoyage des brasques en un seul lavage est difficile. Un lavage en plusieurs étapes à contre courant s'impose. Les études menées sur la lixiviation permettent de prédire correctement l'efficacité de lavage, qui peut ensuite être utilisée dans le cadre d'un modèle de procédé complet développé sur Aspen. Ce procédé complet permet d'obtenir un résidu de brasques ne lixiviant quasiment plus de fluorures, mais aussi de recycler l'eau de procédé. Ce modèle de procédé a été validé en ses points clés par des tests en laboratoire à des conditions proches des milieux industriels.

Finalement, ce travail de doctorat, a mené à plusieurs découvertes clés en ce qui concerne le traitement des brasques : une cinétique de destruction des cyanures, l'étude de l'adsorption des fluorures, mais aussi un design complet de procédé. Il n'existe pas dans la littérature ouverte d'étude aussi scientifique et complète du traitement des brasques.

CHAPITRE VIII

CONCLUSIONS ET RECOMMANDATIONS

Tout d'abord, pour la première fois, une cinétique apparente de destruction des cyanures sur des particules de petites tailles a été déterminée. Ces données cinétiques, très difficiles à obtenir du fait du caractère dangereux des brasques, températures étudiées et temps de réaction rapide, sont un élément essentiel afin de pouvoir procéder à l'optimisation d'un procédé thermique de traitement des cyanures des brasques.

De plus, un mécanisme d'action des additifs anti-agglomérants, soulignant l'importance de la taille des particules, a été suggéré. Ce mécanisme permet la détermination de la proportion optimale d'additifs nécessaires pour éviter l'agglomération.

Afin de compléter l'étude précédente, un modèle de dévolatilisation et de combustion des brasques a été mis au point utilisant un seul set de paramètres cinétiques afin de prédire les réactions dans une grande diversité de conditions. Les 20 000 points générés par le travail expérimental de détermination des paramètres ont permis d'obtenir un modèle robuste susceptible d'être utilisé afin de contrôler la combustion de la fraction carbonée des brasques lors de l'incinération des cyanures. De plus, pour la première fois, ce modèle permet de décrire la perte linéaire de masse observée en fin de réaction de dévolatilisation.

Concernant le traitement des fluorures, la lixiviation des fluorures a été étudiée et les sels de NaF ont été identifiés comme la principale source de fluorures lixiviables. Un modèle d'adsorption du fluor en milieu liquide sur la surface des particules de brasques a été mis au point. L'utilisation de ce modèle a permis de modéliser sur Aspen un procédé complet de lavage des particules de brasques incluant trois étapes et une boucle de recyclage. Le procédé étudié permet de recycler plus de 85% de l'eau de lixiviation. Le procédé obtenu a été validé expérimentalement, et permet de respecter la législation québécoise de lixiviation des fluorures. De plus, un lavage supplémentaire à la soude permet de respecter des normes encore plus sévères.

De plus il a rendu possible des avancées significatives vers le développement de procédés efficaces de traitement des brasques. Les modèles développés vont permettre de faire l'économie des étapes d'essais et erreurs inhérentes au développement de tous procédés de traitement des brasques.

En conclusion, ce travail scientifique contribue à l'avancement de la science sur plusieurs points :

- La démonstration qu'un lit fluidisé circulant interne peut être utilisé pour mesurer des cinétiques de réactions difficiles à obtenir.
- L'utilisation d'une méthodologie rigoureuse afin d'obtenir une cinétique de réaction robuste par thermogravimétrie.
- Le développement d'une isotherme de Langmuir d'adsorption des fluorures sur les brasques dans le cas où le solvant est une solution d'eau acidifiée ou de Na_2SO_4 concentrée.
- Le développement et la validation du logiciel Aspen pour la modélisation de procédé.

Pour étendre la portée des ces travaux, il serait intéressant d'intégrer les cinétiques de combustion et de dévolatilisation ainsi que celle de destruction des cyanures dans un modèle Aspen, afin de l'associer au lavage des fluorures.

Le procédé de lavage des fluorures obtenu sur Aspen, reste à optimiser de façon plus fine. Il serait intéressant de définir un modèle d'adsorption plus complet prenant en compte l'effet de la température, de la force ionique et du pH afin de pouvoir faire varier tous ces paramètres et complètement optimiser le procédé. De plus, inclure dans le modèle de procédé Aspen, la lixiviation de la cryolite permettrait de prédire les conditions nécessaires pour faire diminuer la lixiviation du fluor sous la barre des 50 ppm.

Enfin, une étude devrait être menée sur les types de brasques susceptibles de contenir d'autres espèces dangereuses pour l'environnement (Arsenic, Fer, Aluminium) afin d'étudier le devenir de ces espèces dans le procédé de traitement thermique ainsi que dans la partie lixiviation.

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ANNEXE A :

DESCRIPTION DES PROCÉDÉS DE TRAITEMENTS DES BRASQUES

REVUE DES TECHNOLOGIES DISPONIBLES :

Réutilisation directe des brasques dans l'industrie (pas de traitement):

Valorisation énergétique:

La combustion de brasques dans une unité de combustion de charbon à été rapportée par Givens et al. (1989). Lors des tests, des brasques étaient ajoutées au charbon dans une proportion de 2% en masse. La température de combustion atteinte était de l'ordre de 1200°C et la concentration d'oxygène à l'intérieur de la fournaise était de 4%. Les responsables des tests n'ont remarqué aucune différence de fonctionnement dans l'opération du procédé. Les cyanures sont détruits à 99.93 % lors de la combustion. Des émissions de fluorures sont mesurées à la cheminée et les fluorures des cendres obtenues étaient lixiviables.

Production d'acier:

Les brasques présentent une forte proportion de fluorures et de carbone. Ces deux caractéristiques présentent un grand avantage pour des industries telles que celles de l'acier qui nécessitent de grande quantité de fluor et carbone. Les brasques constituent alors une source de matière première intéressante. Elles sont broyées à 7 mm puis directement additionnées à la matière première lors de l'utilisation des fournaises de fonte dans des proportions de 0.7 à 1 lb par tonne d'acier produit. (Personnet, 1999, Brown and Reddy, 1994, Bourcier et al, 1994; Augood and Keiser, 1989, Lee Byers, 1982). Les cyanures sont automatiquement détruits dans le procédé. Les aciers obtenus présentaient une composition moindre en phosphore et sulfure.

Valorisation énergétique à travers la production de ciment :

Le ciment est composé de CaO-SiO_2-Al_2O_3-Fe_2O_3, des composés déjà présents dans les brasques. Le produit final est obtenu en chauffant un mélange de produits réactifs dans des fours rotatifs à 1500°C.

Les brasques peuvent être exploitées dans l'industrie de production du ciment selon deux approches :

- La fraction carbonée constitue une excellente source d'énergie.
- La fraction de réfractaires peut directement servir comme matière première pour le procédé.

La valeur énergétique des brasques varie de 3000 à 9000 BTU/lb selon leur contenu en réfractaire (Paradis 1998, Brown and Reddy, 1994). Or, l'industrie du ciment est fortement consommatrice d'énergie et le carbone des brasques constitue potentiellement une excellente source d'économie pour ce type d'entreprise. De plus, les fluorures contenus dans les brasques sont reconnus comme ayant un effet accélérant dans le procédé de préparation du ciment.

La partie réfractaire des brasques constitue une matière première de choix pour l'industrie du ciment. Cependant, la composition des réfractaires est déficiente en certains éléments qui doivent être préalablement additionnés alors aux brasques pour les rendre utilisables.

Depuis 1997, Pechiney valorise la fraction réfractaire des brasques (non classées) soit le tiers des brasques usées, dans des fours à ciment. Byers et al. (1986) estime que 20% de la capacité américaine annuelle de production de ciment suffit pour traiter complètement toute la production de brasques

Cependant, utiliser un déchet dangereux dans un procédé autre nécessite d'obtenir un permis d'opération, ce qui est souvent difficile d'autant plus que l'image des cimenteries pourrait être atteinte au niveau de l'opinion publique. Des tests coûteux sont nécessaires afin de prouver l'innocuité du produit. De plus certains effets secondaires pourraient intervenir, comme par exemple une modification de la couleur du ciment. (Alcan, 2002, Byers et al., 1986. Byers and Lee, 1982). Enfin, Kimmerle and al. (1994, 1989) ainsi que Groleman et al (1994) estiment que le ciment ne fait que ralentir la lixiviation des fluorures et ne permet pas une fixation définitive des polluants.

Procédés de lavage ayant pour but la maximisation du recyclage des matériaux.

Alcan : LCLL (Low Caustic Leaching and Liming).

Alcan après de nombreuses tentatives, a mis au point un procédé de traitement des brasques (Alcan 2002, Kimmele et al., 1994) La capacité de l'usine de traitement des brasques en construction sera de 80 000 tonnes par an. Le coût d'investissement attendu est de l'ordre de 91 millions de dollars.

Selon Alcan, les avantages de ce procédé sont les suivants :

- Capacité du procédé d'accepter une variation dans la composition de la brasque usée.
- La capacité du procédé de détruire les cyanures.
- La production d'un résidu solide (carbone et inertes) non dangereux et qui pourrait être enfoui de façon sécuritaire ou utilisé dans d'autres procédés industriels.
- La possibilité de recyclage et de réutilisation des fluorures sous forme de fluorure de sodium.
- La production d'une solution de soude caustique et d'aluminate pouvant être réutilisée dans une usine d'alumine.
- Les coûts d'opération inférieurs en comparaison à un traitement pyrométallurgique
- La quantité de matière destinée à l'enfouissement est inférieure à la quantité de brasque traitée et peut être faible si le marché peut l'accepter tout les tonnages coproduits
- L'utilisation de procédés, de techniques et d'équipements qui sont connus.

Le procédé de recyclage LCLL, illustré à la figure A.1 est constitué de plusieurs étapes :

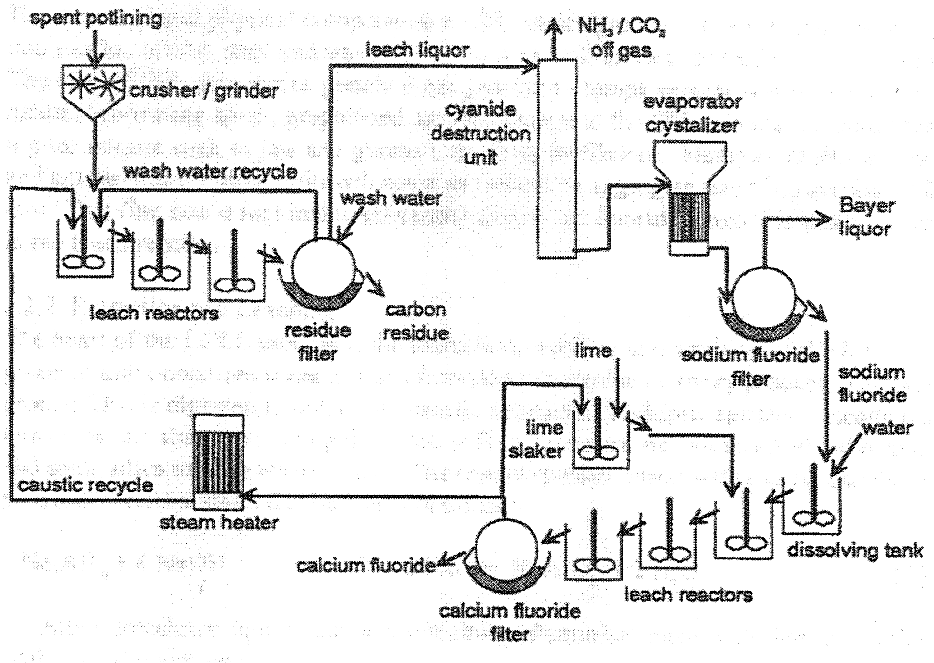


Figure A.1 : Principales étapes de traitement des brasques selon le LCLL (Alcan 2002).

1) La première étape consiste à broyer les brasques usées à une taille variant de 28 à 45 mesh. L'objectif est de récupérer les fractions métalliques contenues dans les brasques. La taille finale obtenue est inférieure à 500 microns.

2) Ensuite, de façon à solubiliser fluorures et cyanures, les brasques sont lavées d'abord à l'eau, puis plusieurs fois dans une solution caustique de soude. Les cyanures, fluorures et certains sels d'aluminium passent alors en solution. Les bassins d'alimentation sont chauffés à l'aide de vapeur d'eau. Les brasques restantes sont alors récupérées par filtration. Ces brasques sont censées être inertes et peuvent être utilisées comme carburant dans des chaudières.

3) Le liquide contenant les fluorures est ensuite chauffé sous pression 1.5 MPa à 180°C afin de réduire la concentration de cyanures à moins de 2 mg/L. Les cyanures sont détruits par hydrolyse.

4) Quatre évaporateurs en série sont utilisés afin d'évaporer la majeure partie de l'eau de la solution. Des cristaux de fluorure de sodium sont alors obtenus. Ces cristaux sont séparés de la solution par filtration. Le liquide porte le nom de liqueur Bayer, contenant aluminium et soude. La liqueur est réemployée dans une autre partie du procédé.

Les détails des réactions chimiques peuvent être trouvés dans les publications de Kimmerle et al., (1994, 1989), Grolman et al (1994), Kasireddy et al. (1996).

La chaudière requise pour produire la vapeur d'eau aura une capacité de 59 000 kW, alimentée au gaz naturel.

Fortin et al (2000) ont étudié une variation possible du procédé LCLL, qui consiste à chauffer la solution de cyanures à l'aide d'une torche au plasma. Le transfert de chaleur est alors assuré par un transfert direct de chaleur et par radiation. De plus, le plasma génère un rayonnement UV qui accélère la destruction des cyanures.

L'avantage du procédé tient au fait que le recyclage complet de tous les produits présents dans les brasques est possible.

Les désavantages résident dans un coût important. Wellwood et al, 1992 identifient les procédés de destruction des cyanures basés sur un lavage, comme étant nettement plus coûteux à opérer et moins efficace. Le LCLL coûterait 130 millions de dollars en investissements. De plus, du fait de son obligation de recyclage, le procédé ne présente pas de flexibilité.

Rethman Lippewerk (Fendel et al., 1996).

L'objectif de ce procédé est de permettre le recyclage complet des fluorures de la brasque en cryolite. (voir figure A.2)

Dans ce procédé, la brasque est d'abord broyée à moins de 10 mm puis à moins de 100 microns. Trois lixiviations successives alcalines dans une solution de soude permettent de récupérer le fluor et le sodium en solution (NaF). Les cyanures de la solution sont détruits par oxydation (Rayons UV et oxygène).

La partie résiduelle des brasques est obtenue par filtration et peut être utilisée comme fuel dans les centrales thermiques ou les fours à ciment. La solution est ensuite filtrée et neutralisée en utilisant une faible quantité d'acide fluorhydrique.

De la cryolite est précipitée en mélangeant la solution de fluorure de sodium obtenue à une solution de fluorure d'aluminium. La fraction solide obtenue par précipitation est ensuite calcinée. La solution est recyclée afin de faciliter le broyage.

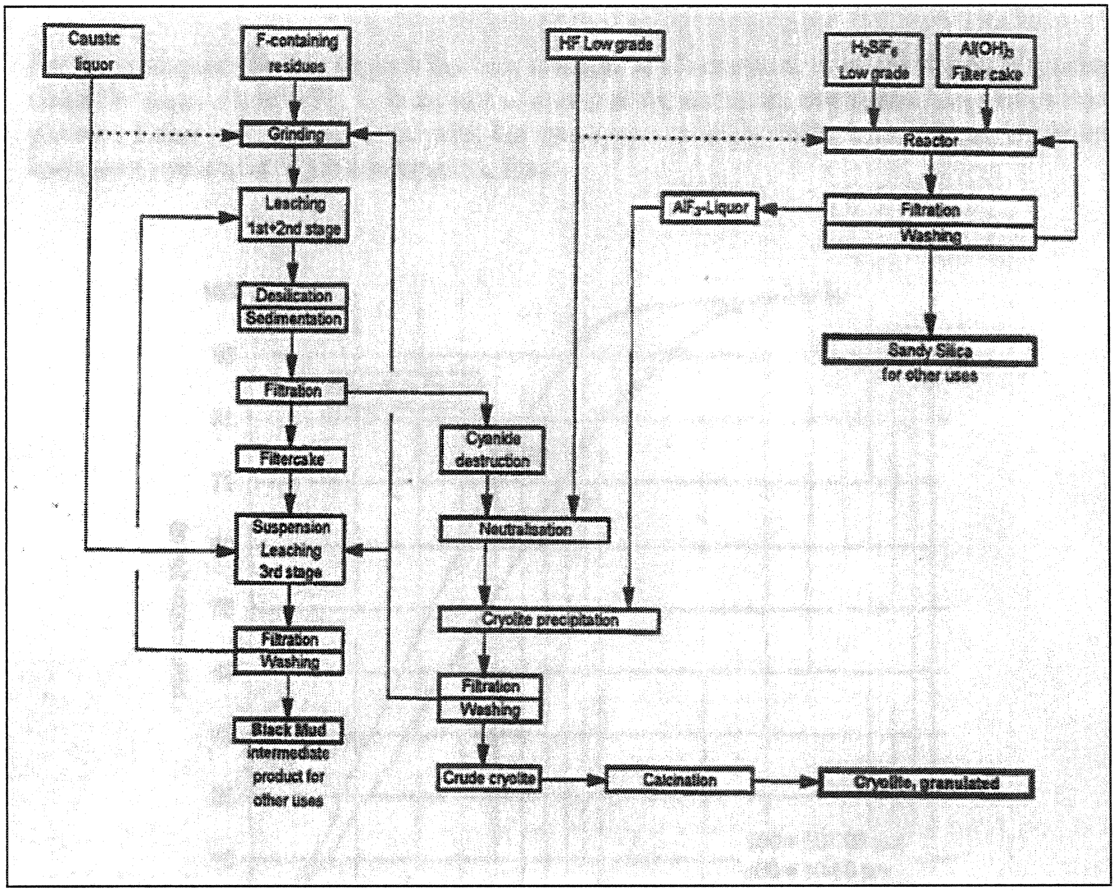


Figure A.2: Description du procédé Lipperwerk (Fendel et al., 1996)

Le coût de traitement d'une tonne de brasques est de 333 $ américain.

Ce genre de procédé a connu de grande difficulté lorsque les nouvelles technologies de filtre à manche ont été introduites dans la production d'aluminium. Cela s'est traduit par des pertes moins importantes de cryolite dans l'industrie de l'aluminium et donc des besoins de productions moins importants. (Bourcier et al., 1994, Jeppet et al. 1996)

Procédé à très hautes températures avec maximisation du recyclage des matériaux:

Procédé de Vitrification Ormet :

Cette technologie a été développée par la compagnie Vortec et est basée sur un procédé appelé 'Cyclone Melting System CMS'. La compagnie Ormet a ensuite acquis les droits de la technologie Vortec afin de construire une usine qui a été mise en opération en 1997 à Hannibal, OHIO traitant 25 tonnes de SPL par jour. Le but de cette technologie est de vitrifier les brasques afin de les recycler dans la fabrication de carreaux de céramiques, de produire des fibres et des granules de bardeaux d'asphalte. (Personnet,1999).

Ce procédé comporte plusieurs étapes (Voir figure A.3):

- Un broyage à une taille inférieure à 40 mesh (400 microns) suivi d'un mélange avec du carbonate de calcium ainsi que du sable. Lors du broyage l'aluminium et l'acier sont récupérés.
- Un préchauffage dans un four vertical à 'Vortex' où l'énergie est fournie grâce à un brûleur gaz naturel. Cette étape de turbulence intense permet l'oxydation des cyanures dans le mélange à une température variant de 1200 à 1500°C.
- Une déposition sur les parois de la suspension gaz-solides à l'intérieur d'un cyclone. Le mouvement rotatif rejette les produits sur les parois pour y former une couche de verre fondu.
- Un trempage dans l'eau du verre fondu afin de générer des granules. Les gaz chauds sont récupérés pour servir à préchauffer l'air d'entrée.
- Les gaz sont ensuite épurés des fluorures et rejetés à l'environnement.

Ce procédé détruit 99.86 à 99.93 % des cyanures et élimine 99.94 % des fluorures.

Les fluorures sont récupérés en faisant circuler le gaz sur de l'alumine (Al_2O_3). L'alumine réagit avec le gaz, pour former du fluorspar (AlF_3). Le produit résultant est vendu ou réutilisé dans la fabrication de cryolite. (Chanania et al. 2000)

Les problèmes liés à cette technologie tiennent à la récupération des fluorures à la cheminée qui est difficile et pose des problèmes importants de fuites. Le coût énergétique est aussi une préoccupation.

Cette technologie a été déclarée BDAT (Best Demonstrated Technology) en l'an 2000. Cela signifie que les normes américaines de traitements des effluents en ce qui concerne les cyanures et les fluorures sont maintenant décidées selon les performances cette technologie.

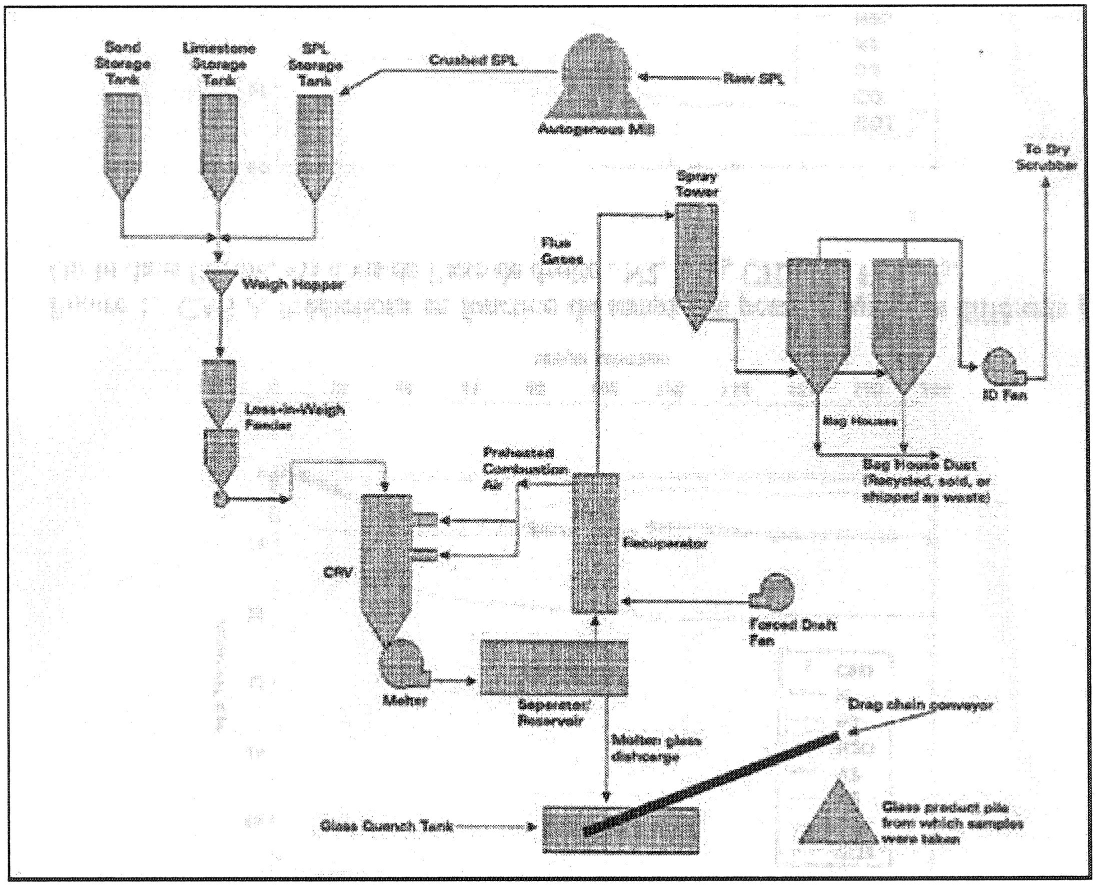


Figure A.3: Procédé Ormet, d'après Chanania et al, 2000.

Au Québec, en juillet 97, la SGF en compagnie de Vortec Corporation et la société Welco Industriale spa ont fondé une société pour promouvoir ce procédé auprès des alumineries québécoises et canadiennes. Après plusieurs années de recherche de partenaire, le projet a été abandonné en février 2002 faute d'intérêt de la part de clients potentiels.

Procédé de Vitrification Ausmelt

Ausmet a mis au point une technologie de traitement utilisant un brûleur submergé dans un bain en fusion (Matusewicz et al, 1996; Jeppe et al, 1996, Guorgi et al, 1994). Cette technologie a servi à l'origine, à traiter des concentrés et minéraux métallurgiques

(Zinc, plomb, étain, Argent, nickel, Platine).

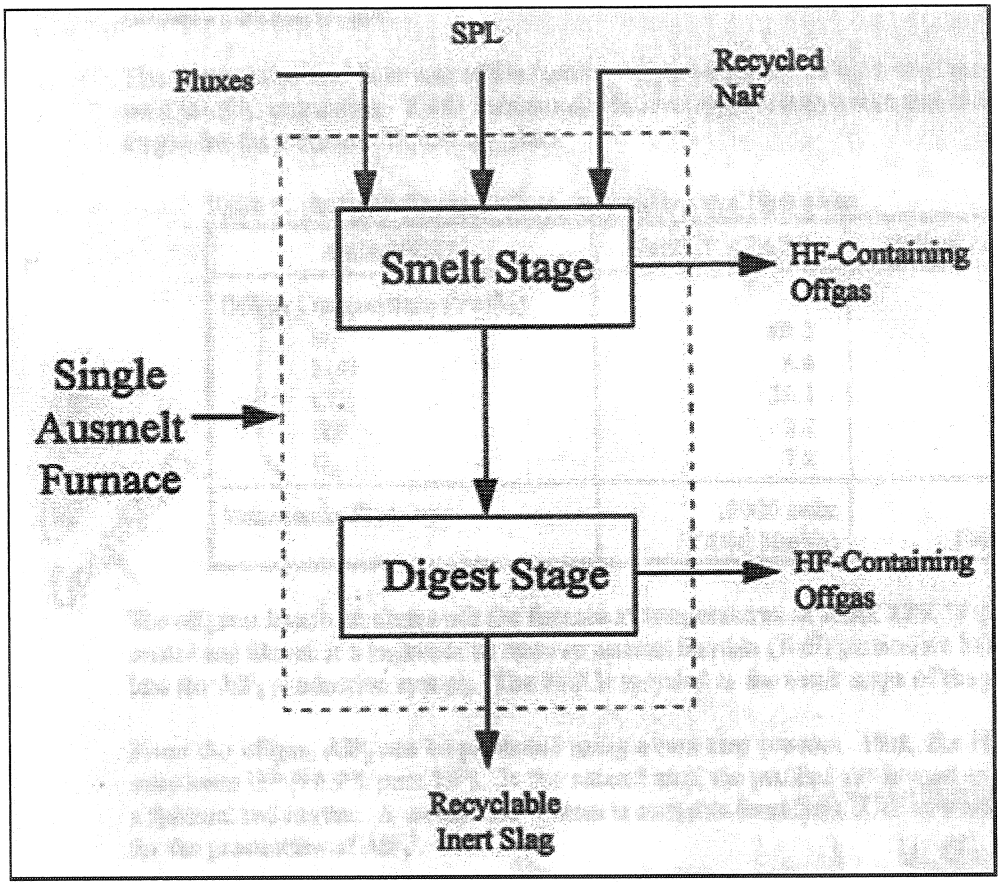


Figure A.4: Description du procédé Ausmelt (Matusewicxz et al, 1996)

Les brasques sont broyées à la taille de un pouce.

Le procédé utilise une technologie batch en deux étapes. Un bain de scories en fusion opérant à une température de 1300°C est utilisé pour détruire les cyanures et volatiliser les fluorures sous forme de HF. Une partie de l'énergie est fournie par la combustion du carbone des brasques. L'unité produit une scorie inerte en quantité similaire à la brasque traitée dont le statut reste à définir. Du calcaire et du fer sont ajoutés à la scorie afin de faciliter la dissolution de la brasque dans le mélange.

Une fois la dissolution terminée, les conditions sont ajustées afin d'améliorer le rejet du HF sous la forme de gaz. Le HF contenu dans les gaz est nettoyé par lavage à l'acide sulfurique puis récupéré et converti en fluorure d'aluminium.

Une unité permettant de traiter 12 000 tonnes de SPL annuellement a été construite et démarrée en 1998 (Personnet,1999). Les essais résidus obtenus de l'unité pilote indiquent une lixiviation de l'ordre de 8 à 55 mg/L des fluors des brasques. Le coût de traitement est de 186 $ par tonne de brasques traitées. Cependant les promoteurs de cette technologie espèrent pouvoir revendre une partie des sous-produits, ce qui abaisserait le coût à 1.84 $ par tonne.

Traitement thermique dans un four rotatif (Reynolds)

Une usine d'une capacité de traitement de 109 000 tonnes de brasques usées a été construite sur ce concept au début des années 90. (Paradis et al.,1998, Pawlek, 1993, Felling and Webb, 1995, Bourcier et al., 1994, Brooks, 1992).

Le procédé consiste à broyer les brasques à un diamètre inférieur à 50 mm, ensuite à mélanger les brasques (40 %) avec du carbonate de calcium (30 %) ainsi que du sable brun (30 %). Le sable brun est du silicate de calcium à la réactivité similaire aux boues rouges provenant des usines de synthèse de l'alumine. L'agglomération est évitée en mélangeant des quantités suffisantes de sables avec les brasques. Le mélange est ensuite alimenté à des fours rotatifs qui mesurent 76 mètres de longueur et 2.85 mètres de diamètre. Ils tournent à des vitesses de 1.24 tours par minute. Le traitement a lieu à des températures variant entre 540°C et 760°C entre l'entrée et la sortie du four rotatif et le temps de résidence est de 90 minutes. Les cyanures sont détruits par oxydation, tandis que les fluorures sont fixés sous la forme de sels de calcium, quasiment insolubles. L'énergie nécessaire au procédé est fournie par des brûleurs à gaz. Le carbone contenu dans les brasques n'est pas oxydé durant le traitement. Reynolds souhaite éviter la combustion des brasques à l'intérieur du four rotatif pour éviter les problèmes d'agglomération.

Les résidus sont ensuite arrosés de chaux et enfouis. Le four rotatif n'émet que très peu de fluorures et cyanures dans les gaz de combustion. Au final, les fluorures sont fixés en CaF_2 et les cyanures détruits dans des proportions de 92 à 94 % par oxydation.

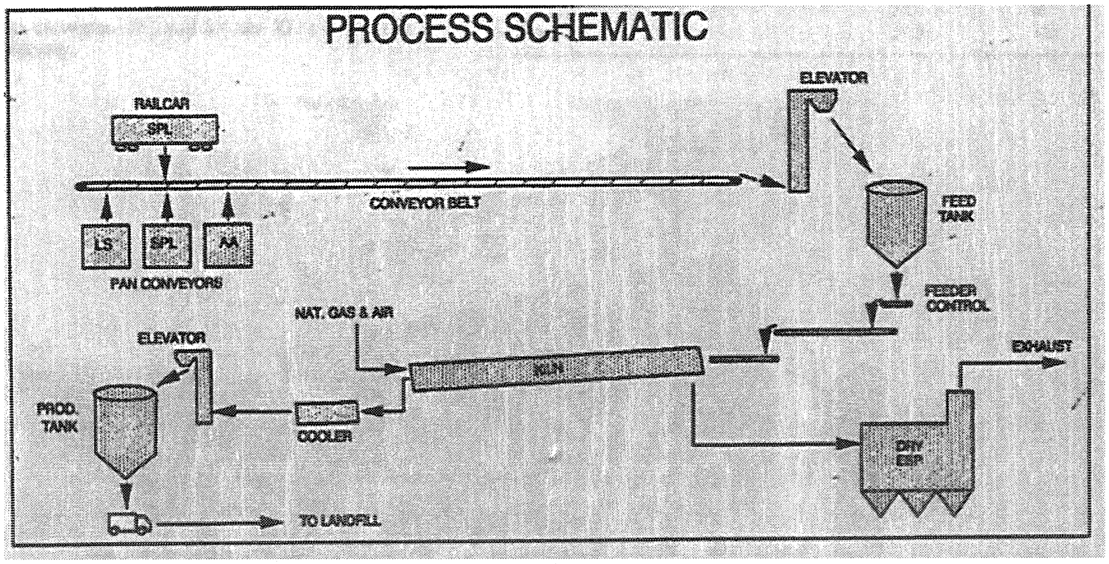


Figure A.5: Description schématique du procédé Reynolds

Les résidus pourraient potentiellement être utilisés à titre d'agrégat d'asphalte et de combustible dans les fours de cimenteries etc… Cependant, ils présentent un caractère fortement basiques (pH de 12 ou 13) et ne sont pas conformes aux critères de lixiviation de l'UPA. En effet les fluorures contenus dans les brasques continuent de lixivier

(Personnet 1999). Kimmerle et al. (1994) estiment que ces problèmes de lixiviation proviennent de la formation de fluorosilicates de calcium à haute température qui sont susceptibles de lixivier à la pluie, mais pas dans des conditions de tests normaux de TCLP. Le résultat est que, même si le résidu était déclassé comme résidus dangereux, les eaux de lixiviation dans les sites d'enfouissement dépassent les normes en ce qui concerne les concentrations des fluors.

Les désavantages de ce procédé sont les suivants :

- Le procédé génère 2.4 tonnes de déchets pour chaque tonne de brasques alimentées.
- Le solide produit ne respecte pas les normes de lixiviation.
- Des quantités d'énergie très importantes sont nécessaires afin de chauffer les brasques (3.1 à 3.6 MMBtu/tonnes de brasques)

Le coût de construction de l'usine au début des années 90, équivalait à 60 millions de dollars américains.

Procédé Comalco (Torbed)

Le procédé Comtor est un procédé en trois phrases (Kidd et al., 1993, Wellwood et al, 1992, Hokins et al, 1995):

- La taille des particules de brasques est d'abord réduite à moins de 1 mm par concassage.

- De l'air chaud (550 à 700°C) est utilisé pour détruire par calcination les cyanures dans un réacteur de type Torbed. Ce type de réacteur est un lit fluidisé avec circulation contrôlée du solide à l'intérieur du réacteur. L'énergie servant à faire monter la température du réacteur ne provient pas des brasques mais est produite par combustion de gaz naturel.
- Traitement de la brasque pour récupérer les fluorures qui peut se faire de deux manières, par fixation ou lavage.

Fixation des fluorures : Le résidu de brasques calcinées peut être mélangé dans un ratio 1 :1 avec de la chaux pour stabiliser les fluorures avant enfouissement. (Kidd, 1993). Les résultats sont très bons, mais la quantité de calcium utilisée est importante et cela augmente la quantité de matériel envoyé à l'enfouissement.

Lavage du fluor : Le fluor est récupéré par lavage des brasques avec de la soude caustique. La solution de soude peut être recyclée sous la forme de Liqueur Bayer (Wellwood and Rodda, 1994). Le fluor peut aussi être potentiellement utilisable sous forme de feldspar (AlF_3) pour des fours à ciments. Les résidus de brasques obtenues ne lixivient que de l'ordre de 25 ppm selon la méthode de TCLP américaine.

Globalement, les cyanures sont détruits à 71 % à 81 % par incinération et le carbone est brûlé entre 30 et 43 % durant la combustion. Le réacteur consomme 1.5 à 3 MJ par kg de brasques traitées.

Une unité pilote a été construite et traite 10 000 tonnes annuellement en Australie à Boyne Islands. Cependant, Kimmerle et al. (1994) rapporte des difficultés d'opération liées à des problèmes d'agglomération. La solution avancée pour régler ce problème tient à un contrôle très strict des températures de fonctionnement.

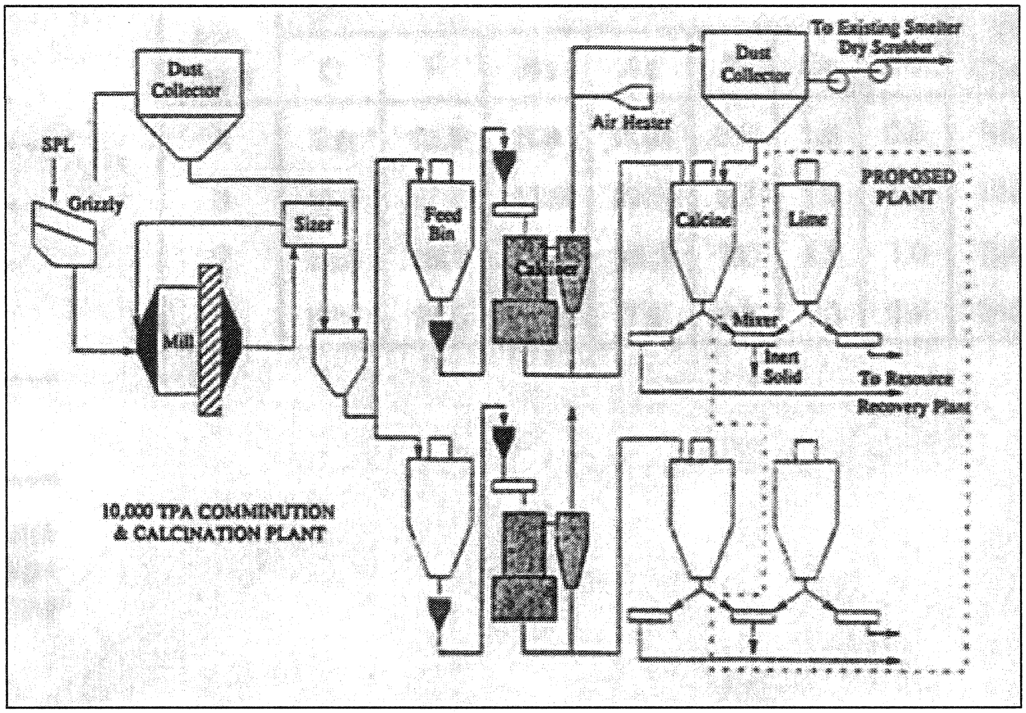


Figure A.6: Description du procédé Comalco d'après Kidd et al. (1993)

Les développeurs préfèrent ne pas fixer les fluorures dans la partie incinération afin de réduire les coûts d'enfouissement et de promouvoir le recyclage des matières premières présentes dans la brasque.

Procédé SPLIT.

Pechiney a mis au point ce procédé en 1991 et bâti une unité pilote d'une capacité de traitement de 3000 tonnes de brasques annuellement. Au cours du procédé, les brasques sont broyées à un diamètre de 2.5 mm puis mélangées avec du sulfate de calcium. Elles sont ensuite introduites dans un réacteur fonctionnant sur le principe du Vortex, équipé d'un brûleur VICARB générant de l'air chaud. Le traitement nécessite la combustion de méthane et propane.

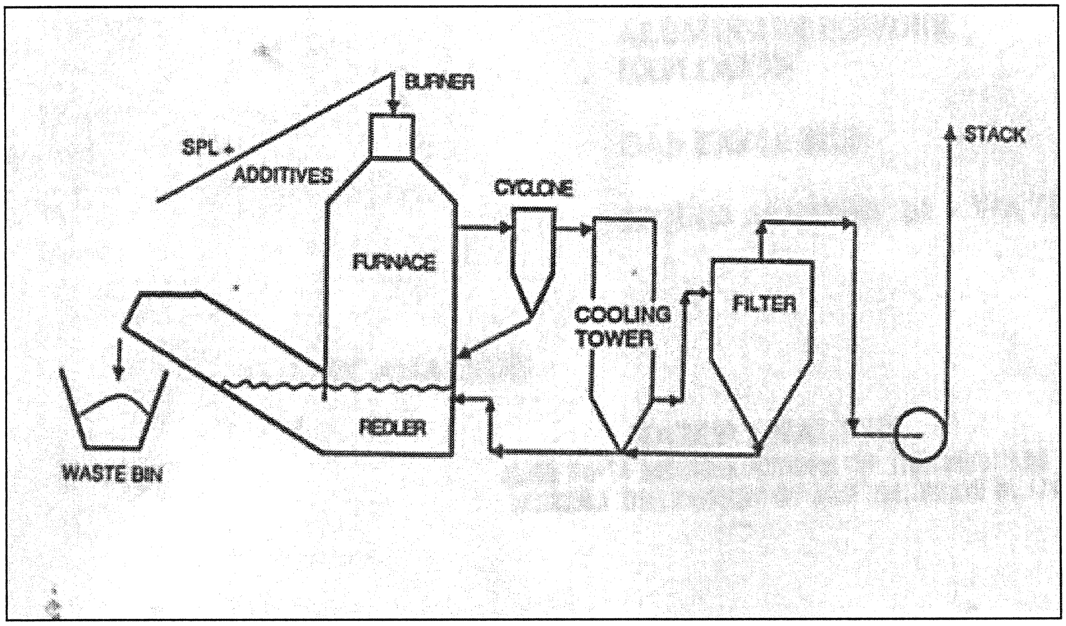


Figure A.7: Procédé Split, d'après Bontron et al., 1992

Les cyanures sont détruits, et les fluorures sont stabilisés. Le temps de résidence est inférieur à 5 secondes. Le carbone n'est pas affecté par le procédé et peu être ensuite utilisé comme source de carburant. (Personnet, 1999, Bontron, 1992).

Procédés incomplets ou non-demontrés :

Deutschman et al. (1987) ont travaillé sur un procédé de lixiviations en séries. Les brasques sont d'abord broyées à une taille inférieure à 20 mm. Les cyanures sont traités par utilisation d'un four rotatif à 350°C. Les résidus de brasques sont ensuite traités par un lavage à l'eau puis un lavage dans des solutions de $CaOH_2$ auxquelles sont ajoutées de l'acide sulfurique. Les fluorures sont précipités sous la forme de CaF_2 mais des sels de $CaSO_4$ précipitent durant l'opération.

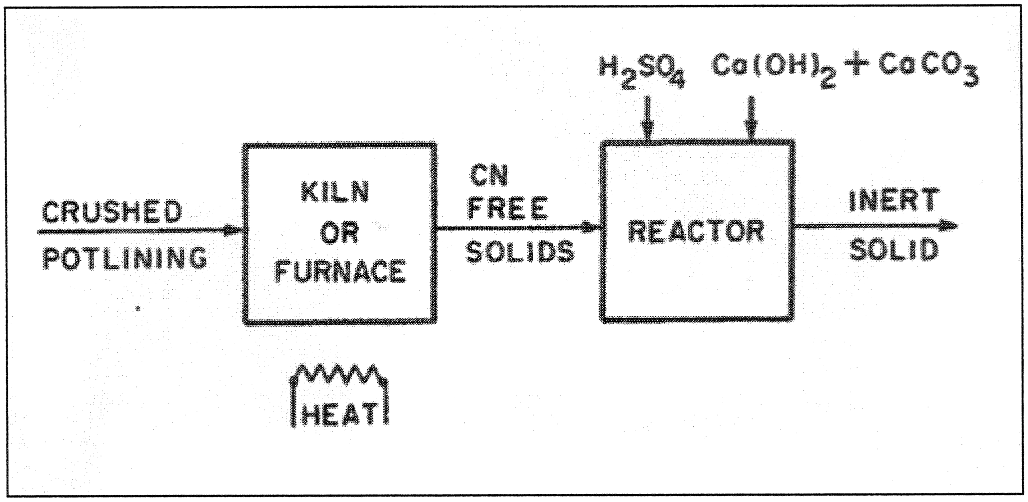


Figure A.8 : Procédé Deutschman

Les cyanures se sont révéles être très difficiles à détruire. L'hydrolyse à haute température ne fonctionne pas et un four rotatif ne permet pas de détruire tout le contenu en cyanures des brasques même après 48 minutes de temps de résidence à 350°C.

Les coûts de traitement sont vaguement estimés à 100 $ US la tonne.

Blayden et al, 1987 ont développé un procédé basé sur le lavage de brasques pour retirer les fluorures solubles et les cyanures. Les brasques sont broyées à 10 mm et subissent un premier lavage à l'eau puis un lavage en solution de $CaOH_2$. Les fluorures sont précipités par du calcium et les cyanures sont traités par utilisation d'hypochlorite de calcium. L'eau est récupérée est recyclée. Le réacteur fonctionne en mode batch, et la quantité de solide à enfouir est de 1.8 fois la quantité de brasques initialement à traiter.

Gnyra et al. (1980) ont mis au point un procédé de lixiviation des brasques dans des conditions très sévères :

Les brasques voient d'abord leurs tailles réduites à 65 mesh. Elles sont ensuite chauffées et mélangées à de l'acide sulfurique entre 180 et 240ºC. Les réactions ayant lieu se traduisent par un fort dégagement d'acide fluorhydrique et de sulfate de sodium. L'acide fluorhydrique est récupéré afin de fabriquer de l'alumine (AlF_3). Les résidus contenant le sulfate de sodium sont ensuite chauffés à 1250ºC afin de réagir avec de la vapeur d'eau pour générer du SO_2. Le SO_2 est ensuite réutilisé pour former de l'acide sulfurique qui est recyclé dans le procédé.

Bush (1986) a développé un procédé basé sur la lixiviation des brasques à l'aide d'un lavage alterné base/acide. Les brasques sont broyées à 11 mm puis lavées à l'aide d'une solution de soude. Une partie du liquide récupéré est utilisée afin de précipiter de l'alumine (AlF_3). La deuxième partie est utilisée pour aider au broyage des brasques

Le deuxième lavage se fait à contre courant avec une solution de sulfate d'aluminium et d'acide sulfurique. L'addition d'acide sulfurique provoque des émissions de cyanures qui sont récupérées et détruites par incinération. Une étape d'élimination du fer par un extractant aliphatique est ensuite utilisée. Le liquide obtenu est ensuite évaporé dans un four rotatif, jusqu'à une concentration de l'ordre de 30% en sulfate de sodium. Le liquide concentré obtenu est ensuite envoyé dans une cellule électrochimique afin de générer de l'acide sulfurique et de la soude.

Le coût de traitement de la brasque est estimé alors de 2767 $ US.

Dahl (1996) rapporte le développement du procédé **Elkem.**

Les brasques sont broyées à une taille inférieure à 15 mm puis sont utilisées dans les procédés de réduction du fer. Elles sont fondues et mélangées au fer. Du quartz est ensuite ajouté au mélange afin de promouvoir une vitrification et d'immobiliser les fluorures. De la vapeur d'eau est projetée sur le liquide afin de générer de l'acide fluorhydrique, qui est ensuite récupéré. L'acide fluorhydrique est utilisé à des fins de génération d'alumine.

Le coût énergétique est de l'ordre de 3.7 MW par tonne traitée.

Si tous les sous-produits sont vendus (fer, alumine, aluminium), le coût de traitement d'une tonne de brasque équivaut à 200 US $.

Pong et al. (2000) ont développé un procédé comprenant quatre étapes, un lavage à l'eau suivi de deux lavages acides et une douche. Chaque lavage requiert un temps de résidence de trois heures. (Adrien et al. 1996)

Premier lavage :

Un lavage à l'eau afin de lixivier les espèces chimiques suivantes : NaF, Na_2CO_3 et CN^-. La solution est ensuite neutralisée à l'aide d'acide chlorhydrique. Les ferrocyanures sont précipités par addition de zinc :

$$Zn^{2+} + Fe(CN^-)_6 \rightarrow Zn_2Fe(CN)_6 \qquad (5)$$

Les cyanures peuvent ensuite être détruits par oxydation.

Les fluorures sont précipités par addition de calcium en CaF_2.

Le deuxième lavage correspond à une étape d'attaque des brasques afin d'en extraire de l'aluminium et des fluorures supplémentaires. L'attaque se fait à l'acide hydrofluorique (HF) à haute concentration (5 à 10 %) en poids.

Le troisième lavage suit le même principe d'attaque acide, mais avec l'addition d'oxyde de calcium supplémentaire afin de fixer les fluorures.

L'auteur estime les coûts de traitement à 100-200 $ la tonne.

Les problèmes de procédé tiennent à la très coûteuse manipulation d'acide et de vapeurs de HCN générées lors des additions d'acide.

Rickman, a travaillé pour la compagnie Ogden à la mise au point d'un procédé de combustion des brasques par utilisation d'un lit circulant fluidisé. (Rickman, 1987; Byers 1986)

Les objectifs étaient les suivants :

- Détruire le contenu en cyanures des brasques.
- Vérifier que la combustion se fait sans agglomération.
- Limiter la lixiviation des brasques.
- Limiter la consommation d'énergie fossile (méthane) à moins de 10% du pouvoir calorifique des brasques.

Lors de ces tests, les particules de brasques sont réduites à une taille de 6 mm. Les brasques sont brûlées à une température proche des 800°C. Un brûleur au méthane additionnel est utilisé afin de maintenant une température élevée dans le réacteur. Le brûleur permet de fournir à peu prés 10 % de la quantité d'énergie nécessaire à la combustion des brasques. L'agglomération est évitée à l'aide d'un additif spécialement développé pour cette application.

Les tests ont permis de conclure que le cyanure était effectivement traité, les fluorures n'étaient pas émis à la cheminée.

Divine (1997) a mis au point une méthode de traitement des brasques à la vapeur. Le traitement commence par le broyage des particules à une taille inférieur de 1 mm. Le procédé fonctionne en batch. De la vapeur d'eau est introduite dans le réacteur à une température de 800°C. Des réactions de gazéification ont alors lieu:

$$H_2O + C \rightarrow CO + H_2 \qquad (6)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (7)$$

À la sotie du réacteur, les métaux sont oxydés, les cyanures sont détruits. Le devenir du fluor n'a pas été étudié. L'auteur suppose qu'ils peuvent passer dans les fumées et être traités soit rester sur le solide. Le gaz produit peut être utilisé comme source d'énergie.

ANNEXE B :

DÉTERMINATION DES CINÉTIQUES DE RÉACTION : REVUE DES MÉTHODES THERMOGRAVIMÉTRIQUES DISPONIBLES:

Introduction

La détermination de cinétique de réaction est un élément essentiel du design et de l'optimisation d'un réacteur. Pour la plupart des applications industrielles, il est impossible de construire des unités pilotes sans posséder de données cinétiques précises. De plus, il est difficile et coûteux de procéder à des tests sur des unités de grandes tailles. Par conséquent des considérations économiques imposent que la cinétique puisse être déterminée de façon peu coûteuse en temps et en moyens. La thermogravimétrie constitue une excellente opportunité d'obtenir une évaluation de la cinétique de réaction, à bas coût. Dans un effort de mise à l'échelle, ces données cinétiques peuvent alors être exploitées dans un modèle hydrodynamique de fonctionnement des réacteurs chimiques afin d'évaluer la conversion du procédé (Lathouwers, 2001; Thunman, 2001, Hastaoglu 1995, Guedes de carvalho et al., 1991).

La thermogravimétrie (TGA) est une technique de mesure qui consiste à suivre le déroulement d'une réaction par la mesure du poids d'un échantillon dans le temps. L'échantillon suivi est placé dans un four dont la température est contrôlée. Il est possible de choisir la composition de l'atmosphère dans ce four. La balance se retrouve généralement sous la forme d'un bras de levier sur lequel l'échantillon est posé. La taille de l'échantillon est très petite, de l'ordre du milligramme, c'est pour cela que la précision de la balance est excellente afin de pouvoir mesurer des variations significatives sur des échantillons dont la masse est initialement très faible. Le système interne de la balance est très délicat, et dans un souci de protection, il est nécessaire de le protéger en insufflant constamment un gaz neutre dans le mécanisme (Argon, Azote...) afin d'éviter le contact avec les gaz chauds corrosifs émis par l'échantillon.

Lors de l'augmentation de température dans le four, la densité des gaz contenus dans la TGA diminue. Sous l'effet de cette diminution de densité du gaz, la poussée d'Archimède exercée sur l'échantillon est modifiée. Par conséquent, le poids apparent sur le bras de levier de la balance change. Afin d'éviter cette perturbation, la balance est calibrée avant chaque série d'expérience avec un blanc, qui consiste en un creuset vide, qui va alors subir ce changement de force et permettre d'en évaluer les effets afin de corriger les mesures prises.

Les mesures en TGA

La quantité suivie lors d'une mesure de TGA est l'évolution du poids de l'échantillon en fonction du temps. On note x la conversion, x =1 en début de réaction et x = 0 en fin de réaction.

La conversion x est définie par l'équation (1)

$$x = \frac{m - m_{initial}}{m_{final} - m_{initial}} \qquad (1)$$

Il est alors possible de définir le taux de réaction par

$$\text{Taux} = \frac{dx}{dt} = \frac{-dm}{dt} * \frac{1}{m_{final} - m_{initial}} \qquad (2)$$

Ce taux va varier selon plusieurs facteurs. Selon une convention bien établie, les effets de la température et de la conversion sur le taux de conversion sont considérés comme indépendant :

$$\text{Taux} = \frac{dx}{dt} = k(T) * f(x). \qquad (3)$$

Où T est la température en degré Kelvin.

k(T) est définie comme la constante cinétique et est souvent représentée par la loi d'Arrhenius :

$$k(T) = k_0 * \exp(-\frac{E.A.}{RT}) \quad (4)$$

k_0 est le facteur pré exponentiel (s^{-1}).
E.A. : est l'énergie d'activation (kJ/mol).
R est la constante des gaz parfait. (J/(K.mol)).
T est la température (Kelvin).

Le terme f(x) est une fonction mathématique de la conversion qui peut prendre une grande variété de forme selon le type de réaction. Un très grand nombre de travaux s'est attaqué aux problèmes de cinétiques et de la détermination de f(x). Même si une grande variété de fonctions f(x) a été établie, celles-ci peuvent être résumées dans un tableau :

Tableau B.1 : Les différentes formes de f(x) dans une expression cinétique

Type d'équation	**f(x)**
Premier ordre	$(1-x)$
Deuxième ordre	$(1-x)^{2}$
Surface contractante	$2*(1-x)^{0.5}$
Volume contractant	$3*(1-x)^{2/3}$
Loi de puissance (m>1)	$m*(x)^{(m-1)/m}$
Avrami-Erofe	$m*(1-x)*(-\ln(1-x))^{(m-1)/m}$
Prout Tompkins	$x*(1-x)$
1-D diffusion	$1/(2*x)$
2-D diffusion	$(-\ln(1-x))^{-1}$

3-D diffusion	$3/2*(1-x)^{2/3}$
Ginstling-Brounshtein	$3/2*((1-x)\ 1/3 - 1)^{-1}$

m étant un paramètre sans signification physique.

Sestak and Berggren. (1971) résume toutes ces expressions en signalant que la forme générale de f(x) est :

$$f(x) = x^m.(1-x)^n.(-\ln(1-x))^p \qquad (5)$$

m, n, p étant des paramètres sans signification physique.

Exploitation des données de TGA

Grâce à l'utilisation d'un four, la température est contrôlable facilement. Il est alors possible de travailler selon deux modes: Isotherme ou non Isotherme.

Le mode isotherme diminue le niveau de difficulté de détermination des paramètres cinétiques, puisque la constante cinétique k(T) ne varie pas durant l'expérience. Donc la détermination de la valeur de l'énergie de réaction nécessite de réaliser plusieurs expériences à des températures différentes, et il est difficile d'identifier un changement de mécanisme (changement d'énergie de réaction) en fonction de la température et de la conversion. De plus, au niveau expérimental, il est difficile d'étudier une réaction dans des conditions parfaitement isothermes, puisque l'échantillon ne peut passer instantanément de la température de la pièce à la température où la mesure doit être faite.

Par conséquent, il est préférable d'utiliser une méthode non isotherme afin de réaliser les analyses. En particulier du point de vue du gain de temps, puisqu'une seule expérience est en théorie suffisante pour déterminer, la constante cinétique et f(x).

Par conséquent, souvent, la température varie en fonction du temps de façon linéaire :

$$T = T_0 + \beta * t. \tag{6}$$

Par conséquent, l'équation (7) est obtenue

$$\frac{dx}{dT} = (\frac{k}{\beta}) * \exp(\frac{-E.A.}{RT}) * f(x) \tag{7}$$

Afin de déterminer l'Énergie d'activation, il est nécessaire de passer au logarithme :

$$\ln(\frac{dx}{dT}) - \ln(f(x)) = \ln(k / \beta) - \frac{E.A}{RT} \tag{8}$$

La forme de la fonction f(x) dépend du mécanisme de la réaction. Afin de déterminer la fonction adéquate, la fonction f(x) doit être choisie au hasard. Puis en traçant le coté gauche de l'équation (7) en fonction de 1/T, les valeurs de E.A. et k peuvent être trouvées en mesurant la pente et l'intercept à l'origine. Le choix de la fonction f(x) est fait en retenant l'expression donnant la meilleure linéarité sur le graphique, ainsi que des valeurs d'énergie d'activation et de constantes cinétiques vraisemblables.

Malheureusement ce choix n'est pas toujours évident et est souvent subjectif.

Plusieurs autres méthodes (Sauerbrunn, Haines, 1995) ont donc été mises au point dans l'hypothèse ou le choix de la fonction f(x) n'était pas aisé :

Méthode intégrale :

La fonction utilisée est g(x) définie par :

$$g(x) = \int \frac{dx}{f(x)} = (\frac{k}{\beta}) * \int \exp(-\frac{E.A}{RT}) dT \qquad (9)$$

Or,

$$\int \frac{-E.A}{RT} = (\frac{E.A}{R}) * \int \exp(\frac{-z}{z^2}) dy = \frac{E}{R} * j(z) \qquad (10)$$

$$\text{Avec } z = \frac{E.A}{RT} \text{ et } j(z) = \frac{\exp(-z)}{z^2} \qquad (11)$$

De nombreuses méthodes existent pour simplifier ce problème dont la méthode de Coats and Redfern (1964) ou Lee and Beck (1984).

'Reduced time plots.'

Méthode isotherme basée sur la détermination du mécanisme en fonction de la forme de la courbe.

Méthode des taux de réaction constants.

Dans cette méthode, la température de l'échantillon est variée (au point même de refroidir l'échantillon), afin de maintenir un taux de réaction constant.

Rampe de chauffage dynamique

Dans ce type d'expérience, au fur et à mesure que la réaction a lieu, le taux de chauffage diminue afin d'obtenir une meilleure précision sur les données durant les moments clés de la réaction.

Isotherme à seuils.

La température augmente jusqu'à ce que le taux de réaction atteigne une certaine valeur. La température cesse alors d'augmenter jusqu'à ce que le taux de réaction descende en dessous d'un certain seuil. Par conséquent, lors de cette mesure, l'expérience est constituée d'un ensemble de mesures isothermes séparées par des montées en température.

Analyse alternative des données de TGA.

Quelle que soit la façon dont les données TGA sont obtenues, il est souvent extrêmement difficile d'optimiser le choix de la fonction f(x). De nombreuses méthodes sont utilisées pour arriver à cette fin (Haynes, 1995), cependant toutes présentent des biais qui rendent souvent peu crédibles les résultats obtenus à moins que d'autres données cinétiques obtenues autrement viennent confirmer certaines hypothèses prises (Conesa et al., 2001; Smiezk et al., 1982, Antal et al.1997, Arnold et al., 1982)

Un exemple des ces incertitudes trouvées lors de l'analyse de données cinétiques de dévolatilisation et combustion peut être rencontré dans le cas de l'étude de la cinétique de combustion de paille de riz. (Mansaray and Ghaly, 1997,1998,1999a et b; Jain 1999). Ces études montrent clairement la très grande diversité des données cinétiques obtenues malgré les similitudes dans les expériences menées. Vraisemblablement des problèmes liés à l'analyse de données perturbent les résultats.

Les données cinétiques obtenues peuvent provoquer des débats scientifiques très passionnés, d'une durée de plusieurs années dépendamment de la méthode d'analyse utilisée et de données scientifiques qui se contredisent. (Chornet and roy, 1979; Agrawal, 1985)

Lorsque qu'il devient difficile d'obtenir une bonne évaluation pour f(x) en utilisant des méthodes traditionnelles ou en améliorant la précision des données obtenues, il est commun d'avoir recours à des modèles plus complets d'analyse de cinétiques :

Wilburn (1999,2000) démontre que deux réactions ayant lieu de façon quasi-simultanées paraissent constituer une réaction unique sur les données de TGA. Mais les données cinétiques obtenues ne sont pas analysables par une approche classique de résolution. Il faut souvent diminuer la vitesse de rampe de chauffage et connecter la TGA à un spectromètre de masse pour obtenir des données supplémentaires permettant l'analyse.(Materazzi, 1998; Evans, 1987)

Cependant, globalement, lorsque l'analyse des données s'avère problématique, deux grandes écoles de pensée s'affrontent :

- La première estime que les données cinétiques obtenues par TGA représentent exactement la réaction chimique ayant lieu sans perturbations liées au milieu de mesure (transfert de masse et de chaleur). Selon cette école de pensée, la clé pour augmenter la qualité du fit entre les données expérimentales et d'éventuels modèles réside dans l'amélioration des expressions théoriques utilisées afin de décrire les réactions (Sestak and Berggren, 1971; Chornet and roy, 1979)

- La deuxième école de pensée estime que les principaux problèmes sont liés à des problèmes de réglage de la TGA et d'imperfections des mesures, qui peuvent être compensés afin d'en retirer les données cinétiques réelles. Selon cette école, en modélisant les effets des problèmes de transfert de masse et de chaleur, il est possible d'arriver à retirer leurs effets des données cinétiques et d'en déduire la cinétique réelle (Antal et al., 1997; Agrawal, 1985, Di blasi, 1996, 1997,2002)

Modification des lois cinétiques.

Dans la première école, les problèmes de transfert de chaleur et de masse sont négligés. L'hypothèse est toujours faite que la taille de particules peut être rendue suffisamment petite afin d'éliminer toutes ces imprécisions. Cette réflexion est appuyée sur des calculs théoriques du même genre que ceux présentés par (Janse et al., 1998) dans le cas de la combustion de particules dans une atmosphère d'oxygène :

La quantité d'énergie maximale (Qmax) à évacuer par seconde peut être calculée :

$$Q\max(produite) = Vp * \rho_0 * \Delta H * r_{\max} \qquad (11)$$

La quantité d'énergie qui peut être éliminée par convection par les particules est :

$$Q\max(é\lim inée) = h * A * (T_p - T_{gas}) \qquad (12)$$

Quand l'équilibre est atteint, les deux quantités de chaleur sont égales.

Si la température augmente de ΔT_{rmax} , le taux de réaction maximale peut être évalué par

$$r\max = k_0 * \exp(\frac{-E.A}{R(Tgaz + \Delta T)}) \qquad (13)$$

En combinant les équations 11 à 13, une expression de ΔT est obtenue et donc l'augmentation de température des particules en fonction du volume des particules peut être évaluée. Il est alors possible de jouer sur le volume des particules de façon à réduire au minimum la différence de température.

Si les modèles ne prédisent toujours pas adéquatement les résultats expérimentaux, c'est que les expressions choisies ne conviennent pas. Il faut alors modifier les expressions cinétiques (voir équation (4)). Une approche très commune consiste à supposer que la constante de réaction n'obéit pas à la loi d'Arrhenius mais à une autre loi de la forme :

$$k = k_0 T^m \qquad (14)$$

Le facteur m dépendrait directement du nombre de sites actifs présents sur la particule. Sous l'effet de l'augmentation de la température, le nombre de sites actifs augmente, et cette augmentation est proportionnelle à une puissance de la température et pas à une exponentielle de la température (Sharma et al., 1998, Arnold et al., 1982).

Une autre modification très commune, consiste à dire que le mécanisme de la réaction est transformé une fois un certain degré de conversion atteint. Par exemple, les sites de surfaces ne réagiraient pas comme les sites se trouvant au cœur de la particule. En poussant cette idée à l'extrême, il est possible de supposer que les énergies d'activation vont obéir à une loi de distribution, supposée gaussienne. Chaque énergie d'activation correspondra alors à des sites plus ou moins difficiles d'accès.

$$k = \int_{e=0}^{e=\infty} k_0 * \exp(\frac{E.A.}{RT}) * i(e)de \qquad (15)$$

Avec i(e) qui représente la probabilité d'une énergie d'activation, c'est à dire, la probabilité d'un type de site sur la particule.

Anthony et al.(1975) ont été les premiers à faire ce genre d'hypothèse pour expliquer la pyrolyse du charbon. Ses applications se sont beaucoup étendues depuis à de nombreuses analyses cinétiques. (Please et al., 2003; Vogel, 2002)

Pour les tenants de la seconde école de pensée, les paramètres de transfert de masse et de chaleur ne peuvent être négligés. Leurs importances sont minimisables dans les applications de thermogravimétrie, mais ne peuvent être négligées lors de la modélisation de cinétique dans la plupart des unités industrielles. Par conséquent, ces phénomènes doivent être pris en compte :

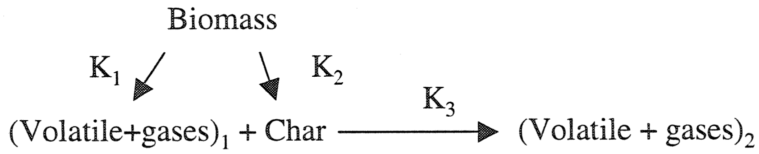
Deux types de limitations peuvent exister dans une expérience de TGA :

1) Limitation due au transfert de matière, lié à des problèmes de diffusion, intra et extra particulaire.
2) Limitation due au transfert de chaleur, lié à la différence de température de l'échantillon par rapport à celle du four.

Pour réduire la première limitation, la taille des particules est réduite et les quantités de réactifs introduits dans la TGA sont diminuées. La seconde limitation est contournée en réduisant l'augmentation de température dans le temps.

Cependant, dans les cas d'étude de pyrolyse, ces deux options ne sont pas intéressantes :

Un des schémas de réactions les plus employés pour l'étude de la pyrolyse est utilisé par Koufopanos (1991) :



Les volatiles émis durant la pyrolyse réagissent de nouveau avec le char formé par la pyrolyse pour donner d'autres volatiles et chars.

Cet aspect des réactions de pyrolyse est très important et modifie complètement les rendements respectifs de volatiles, gaz et char en fin de réaction. Ces rendements vont dépendre directement du temps de résidence des volatiles en contact avec le char. Il est donc important que ce temps de résidence soit évalué. Si la taille de l'échantillon est réduite, le temps de résidence des volatiles est très faible et les réactions secondaires ne sont pas observées. La cinétique de réaction est alors biaisée vers la formation de volatile et de gaz.

De plus, la stabilité des gaz est modifiée par la température. Si la température est faible lors de l'émission des volatiles, ces derniers peuvent se condenser et n'ont pas tendance à être craqués. Or dans un réacteur industriel, la montée en température est très rapide (1000 K/s dans un lit fluidisé est possible). Par conséquent la distribution des produits de réaction est totalement différente dans le cas de la balance thermogravimétrique, par rapport à un réacteur industriel.

Par conséquent, afin d'obtenir des données significatives, il est important de réussir à prédire les cinétiques de TGA pour des échantillons de taille importante, et des montées en température rapides.

Prendre en compte tous ces problèmes de transfert de masse et de chaleur doit être un objectif prioritaire dans la détermination de cinétique. De nombreux modèles peuvent être construits sur cette base. Cependant seules quelques équipes utilisent un modèle complexe pour prendre en compte les problèmes de diffusion.

Prise en compte des phénomènes de transfert de masse et de chaleur.

La plupart des équipes de recherche se consacrent aux problèmes de prédiction de transfert de chaleur. Une TGA est limitée par la quantité de chaleur transférée aux particules par minute. Cette limite se situe généralement aux environs de 50 K/min. Souvent, les taux de transfert de chaleur utilisés sont encore plus faibles, de l'ordre de 10 à 20 K/min. Or les taux de transfert de chaleur industriels sont plutôt de l'ordre de 1000 K/s pour le cas des lits fluidisés par exemple. Par conséquent afin d'avoir des taux de transfert de chaleur plus proches de la réalité industrielle, plusieurs design de réacteurs à hausse de températures très rapide ont été utilisés (chauffage par laser, hausse de température forcée par un fil électrique porté au rouge etc...). Par conséquent, la plupart des équipes de recherche se préoccupant des limitations de la TGA ont consacré leur effort aux problèmes de transfert de chaleur.

Transfert de chaleur seulement :

Pyle and Zaror (1984) ont résumé les efforts de différents groupes de recherche en prédisant qu'il existe quatre zones permettant de définir le contrôle de température. Ces zones sont définies en fonction de trois chiffres adimensionnels :

$$Py = \frac{h}{k\rho C_p Rp} \tag{16}$$

$$Bi = \frac{hRp}{k_T} \tag{17}$$

$$Py' = \frac{k_T}{k\rho C_p Rp^2} \tag{18}$$

Les quatre zones correspondent à quatre zones de modélisation :

Zone IV : Bi>1, Py<1, Py'>1
La réaction est contrôlée par le transfert de chaleur interne (shrinking core).

Zone III : Bi<1, Py'>1
La réaction est contrôlée par la cinétique intrinsèque.

Zone II : Bi>1, Py'<1
La réaction est contrôlée par transfert de chaleur externe.

Zone I : Cas général, aucun mécanisme ne domine.

Dans tous les cas, le transfert de masse est négligé et est supposé immédiat et ne pas limiter la réaction.

Transfert de chaleur et prise en compte empirique du transfert de masse

Des modèles plus sophistiqués ont ensuite été mis au point tel que celui de Koufopanos, (1984) qui a bâti un modèle basé sur une seule particule soumise à une limitation du transfert de chaleur. Les problèmes de transfert de masse sont pris en compte par un coefficient empirique.

Les équations de ce modèle sont les suivantes

Bilan d'énergie :

$$\frac{\delta(\rho C_p T)}{\delta t} = -(\nabla . q) + (-\Delta H)(-\frac{\delta \rho}{\delta t}) \qquad (19)$$

En supposant que la chaleur est transmise uniquement par conduction à l'intérieur de la particule :

$$qr = -k_t(\frac{\delta T}{\delta r}) \qquad (20)$$

L'équation (21) est alors obtenue :

$$\frac{\delta(\rho CpT)}{\delta T} = (\frac{1}{r}) * \frac{\partial(rk_t * \frac{\delta T}{\delta r})}{\partial r} + (-\Delta H) * (\frac{-\delta \rho}{\delta t}) \qquad (21)$$

Les hypothèses suivantes sont prises :

1) Densité (ρ), Chaleur spécifique (Cp), Conductivité thermique (k), sont supposés constants.
2) t= 0, $T(r,0)= T_o$.

3) t>0, r= 0, $(\frac{\partial T}{\partial r}) = 0$ r = R, $-k(\frac{\partial T}{\partial r}) = h(T - Tf) + \varepsilon_1 \sigma (T^4 - T_f^4)$

Il ne manque au système qu'une hypothèse de mécanisme de réaction :

Pour m, masse de biomasse

$$\frac{dm}{dt} = (-K_1 + K_2) * m^n \tag{22}$$

$$\frac{dm_1}{dt} = (K_2 m^n - K_3) * m_1^n \tag{23}$$

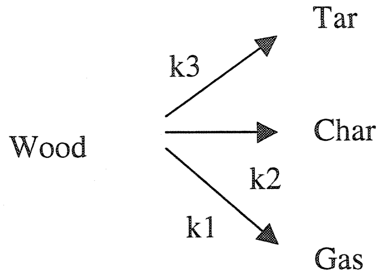
$$\frac{dm_2}{dt} = \alpha * m_1 \tag{24}$$

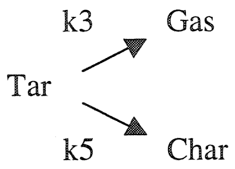
Avec, une réaction d'ordre m pour la pyrolyse initiale. Les deux autres réactions de pyrolyse présentent un ordre 1.

Le transfert de chaleur est très bien pris en compte dans ce modèle, cependant, le coefficient alpha est le seul paramètre lié au transfert de masse. Ce coefficient est fonction du temps de résidence du gaz aux alentours de la particule. Plus le temps de résidence est élevé, plus alpha est grand. C est un coefficient empirique qui est déterminé expérimentalement.

Transfert de chaleur et transfert de masse modélisés

Di blasi (1996) a mis au point le modèle le plus complet de dévolatilisation de particules de bois, en tenant en compte des transferts de chaleur et de masse. Malheureusement, son modèle n'est pas appuyé par des résultats expérimentaux.





Pour la phase solide, il est possible d'écrire :

Pour le bois :

$$\frac{\delta \rho_w V}{\delta t} = -(k_1 + k_2 + k_3)\rho_w V \tag{25}$$

Pour le char :

$$\frac{\delta \rho_c V}{\delta t} = -k_3 \rho_w V + k_5 \rho_T V_t \tag{26}$$

avec

$$\rho_w = \frac{M_w}{V} \qquad \rho_c = \frac{M_c}{V} \tag{27}$$

qui représentent les densités du bois et du char.

À l'aide d'un bilan de masse sur le goudron (tar), on obtient :

$$\frac{\delta\varepsilon\rho_T}{\delta t}+\frac{\delta(\rho_T u)}{\delta x}=\frac{\delta}{\delta x}(D*\rho_g\frac{\delta Y_T}{\delta x})+\omega_T-\frac{\rho_T\varepsilon}{V}\frac{\delta V}{\delta t} \qquad (28)$$

et sur le gaz :

$$\frac{\partial\varepsilon\rho_g}{\partial t}+\frac{\partial u\rho_g}{\partial t}=\omega_g-\frac{\rho_g\varepsilon}{V}\frac{\partial V}{\partial t} \qquad (29)$$

Le bilan de chaleur obtenu à partir des chaleurs de réaction permet d'obtenir l'équation suivante :

$$\frac{\partial}{\partial t}(\rho_c h_c+\rho_w h_w+\varepsilon(\rho_g h_g+\rho_T h_T))+\frac{\partial}{\partial x}((\rho_T h_T+\rho_g h_g)u)=\frac{\partial}{\partial x}(k*\frac{\partial T}{\partial x})+\sum_{k=1}^{k=3}r_k h_k+\sum_{i=4,5}r_k\Delta h_k$$
$$-\frac{\rho_c h_c+\rho_{wh_w}+\varepsilon(\rho_g h_g+\rho_T h_T)}{V}\frac{\partial V}{\partial T} \qquad (30)$$

avec u est la vitesse,

$$u=\frac{K}{\mu}\frac{\partial P}{\partial x} \qquad (31)$$

$$P=\frac{\rho_g RT}{W_g} \qquad (32)$$

Les constantes de réactions sont définies par la fonction d'Arrhenius :

$k_k=k_{0k}\exp(-\frac{E.A_k}{RT})$ k variant de 1 à 5. (33)

$r_k=k_k\rho_w$ k variant de 1 à 3. (34)

$r_k = k_k \rho_T$ k variant de 4 et 5. (35)

Les émissions de goudrons et de gaz sont définies de la façon suivante :

$$\omega_T = k_2 \rho_w - \varepsilon (k_4 + k_5) \rho_T \tag{36}$$

$$\omega_g = (k_1 + k_2) \rho_w - \varepsilon (k_5) \rho_T \tag{37}$$

La conductivité thermale effective est exprimée en fonction du carbone initialement présent et du char récemment formé :

$$k^* = \eta k_w + (1-\eta) k_C + \varepsilon k_g + 13.5 \sigma T^3 \frac{d}{\omega} \tag{39}$$

Où $\eta = \dfrac{M_w}{M_{wo}}$ (40)

La diffusivité est aussi exprimée en terme de diffusivité effective :

$$D^* = \varepsilon D \tag{41}$$

Le modèle obtenu est très complexe et requiert de nombreux paramètres. Par conséquent, il est difficile de vérifier sa validité dans le cadre d'expériences de TGA.

De façon générale, la deuxième école de pensée se retrouve avec des systèmes d'équations excessivement difficiles à résoudre. Par conséquent il est commun de poser que l'ordre de la réaction étudiée est 1. Toutes les réactions sont alors modélisées comme des réactions d'ordre 1. Cela simplifie singulièrement une partie des calculs.