Titre: Title:	Rheological behavior of bauxite-and alumina-based castables
Auteur: Author:	Fangbao Ye
Date:	2004
Type:	Mémoire ou thèse / Dissertation or Thesis
Référence: Citation:	Ye, F. (2004). Rheological behavior of bauxite-and alumina-based castables [Thèse de doctorat, École Polytechnique de Montréal]. PolyPublie. https://publications.polymtl.ca/7458/

URL de PolyPublie: PolyPublie URL:	https://publications.polymtl.ca/7458/
Directeurs de recherche: Advisors:	Michel Rigaud
Programme: Program:	Non spécifié

UNIVERSITÉ DE MONTRÉAL

RHEOLOGICAL BEHAVIOR OF BAUXITE- AND ALUMINA-BASED CASTABLES

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ÉCOLE POLYTECHNIQUE

THÈSE PRÉSENTÉE EN VUE DE L'OBTENTION

DU DIPLÔME DE PHILOSOPHIAE DOCTOR (Ph.D.)

(GÉNIE MÉTALLURGIQUE)

MAY 2004

Your file Votre référence
ISBN: 0-612-98187-8
Our file Notre référence
ISBN: 0-612-98187-8

UNIVERSITÉ DE MONTRÉAL

ÉCOLE POLYTECHNIQUE DE MONTRÉAL

Cette thèse intitulée :

RHEOLOGICAL BEHAVIOR OF BAUXITE- AND ALUMINA-BASED CASTABLES

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En vue de l'obtention du diplôme de : Philosophiae Doctor

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ACKNOWLEDGEMENTS

First, I would like to express my sincere gratitude to my supervisor, Prof. Michel Rigaud for his expert guidance, valuable advice, and constant support and encouragement during this Ph.D program at Ecole Polytechnique de Montreal. At the same time, heartful appreciations go to my co-supervisor, Prof. Zhong for his direction, strong support and constant encouragement, for long time at Zhengzhou University.

I gratefully acknowledge Prof. Claude Allaire for his expert guidance and enlightening advice.

Special thanks to Dr. H. He, Dr. S. Palco, Mr. V. Kovac and Dr. E. Paransky for their valuable help and kind suggestions on my work. Sincere thanks to my friendly colleagues at CIREP, Dr. S. Afshar, Dr. E. Divry, Dr. K. Sankaranarayanane, Mr. X. Zhou, M. Zhang and J. Gao for their help and valuable discussion in all aspects.

Sincere thanks to J. P. Bouchard, T. Crisson and H. Rioux at CIREP for their technical and secretarial helps.

I wish to underline my appreciation to my colleagues, Mr. Q. Jia and Mrs. X. Liu for their help and support in experimental work, and also to thank my friendly colleagues at Zhengzhou University, Dr. H. Zhang, C. Ma, M. Liang, E. Xu and T. Ge for their concern, help and valuable discussion.

Of course, I have to also express my deepest appreciation to my wife and son for their love, sacrifice, encouragement and constant support to my study.

RÉSUMÉ

Cette thèse résulte d'un projet de collaboration entre l'École Polytechnique de Montréal et l'Université Zhengzhou (Chine) initié en l'an 2000. Ce projet était articulé sur cinq études :

1) les propriétés rhéologiques des bétons réfractaires à base de bauxite, partie matrice ;
2) les propriétés rhéologiques des bétons réfractaires à base de bauxite et de carbone de Silicium (SiC);
3) les propriétés thermomécaniques de ces bétons;
4) le comportement rhéologique des bétons haute alumine, sans et avec addition de graphite, à basse teneur en ciment;
5) le comportement rhéologique des bétons haute alumine, avec addition de magnésie et de graphite, mais sans ciment.

Initialement, il s'est agi d'optimaliser les paramètres régissant le comportement de la partie matrice d'un béton, contenant jusqu'à 80% de solide (influence de fines de silice et d'alumine, du rapport eau/ciment, de la nature et du pourcentage de dispersant utilisé, de la taille des poudres utilisées). Une fois établi, il s'est agi d'appliquer les résultats aux 2ème et 3ème sujets pour comprendre les relations entre comportement rhéologique et propriétés thermomécaniques de bétons conventionnels de bauxite –SiC, utilisés dans l'industrie du fer. Les 4ème et 5ème sujets ont été abordés pour appliquer les connaissances acquises à de nouveaux bétons, contenant du carbone et de la magnésie.

Les buts de la thèse ont été d'identifier les paramètres qui influencent la fluidisation ou l'épaississement des bétons lors des mélanges, en mesurant les caractéristiques rhéologiques :

viscosité dynamique et limite d'écoulement pour des bétons auto-coulants et pompables, et d'évaluer les conditions optimales pour la formulation des mélanges, incluant ces nouveaux bétons réfractaires contenant du carbone, et notamment du graphite.

Au total, au delà de 200 mélanges ont été préparés et leur comportement rhéologique étudié. À cet effet, trois méthodes expérimentales ont été utilisées :

- un viscosimètre classique pour l'étude des barbotines,
- une table vibrante pour mesurer le degré d'auto-écoulement,
- un viscosimètre IBB pour l'étude des mélanges complets de bétons.

Certains bétons ont en outre été caractérisés au point de vue mécanique, en mettant en œuvre des méthodes conventionnelles de mesures de module de rupture en flexion, à froid et à chaud, d'efforts-déformation jusqu'à rupture, ainsi que des mesures des modules résiduels après chocs thermiques pour évaluer la résistance aux chocs thermiques.

Les travaux se sont déroulés :

1) en contrôlant la quantité totale et le rapport des ultra-fines d'alumine et de microsilice,
2) en contrôlant la distribution granulométrique des particules,
3) en sélectionnant le dispersant approprié,
4) en ajustant le rapport eau/ciment,
5) en ajustant le pourcentage des additifs : SiC, MgO et/ou micro-boulettes de graphite selon le cas.

L'ensemble de ces études a été divisé en 3 chapitres. Il a donné lieu à la préparation de sept articles dont 4 ont déjà été publiés et un le sera en Août, les deux autres devant être soumis sous peu.

Les résultats obtenus sont les suivants :

I) Pour l'étude du comportement rhéologique des bétons à base de bauxite, partie matrice.

1) Parmi les paramètres étudiés : pourcentages d'alumines fines et de microsilice, rapport eau/ciment, dispersants, taille des fines de bauxite, ce sont les fines (d'alumine et de silice) et les dispersants qui ont le plus d'influence sur la viscosité et les taux de cisaillement des barbotines.
2) La viscosité des barbotines décroît avec le pourcentage de microsilice utilisé, mais croît légèrement avec addition d'alumine. Dans chaque cas, le comportement rhéologique des barbotines est celui d'un fluide type Bingham.
3) Parmi les dispersants utilisés, c'est le polycarboxylate-éther qui est le plus efficace pour réduire la viscosité et la limite d'écoulement des barbotines. La quantité à utiliser est de 0.2% poids.
4) La viscosité apparente et la limite d'écoulement croît légèrement lorsque le rapport eau/ciment décroît de 19 à 2.

Ces résultats délimitent les zones de composition d'une matrice pour un béton bauxitique avec des propriétés rhéologiques adéquates.

II) Pour l'étude du comportement rhéologique des bétons de bauxite - SiC.

1) Les bétons bauxitiques contenant du SiC, du ciment alumineux et de la microsilice, ont des caractéristiques de fluidification plutôt que d'épaississement, lors des mélanges et suivent le comportement d'un fluide de type Bingham.
2) Lorsque les additions de SiC vont croissantes, de 0 à 16%, les propriétés rhéologiques des bétons se dégradent au point où la quantité recommandable doit être comprise entre 4 et 8% poids.
3) Dans ces bétons, à base de bauxite et de SiC, l'influence du ciment sur la rhéologie est très faible, tant qu'il s'agit de bétons à ultra-basse teneur en ciment. Pour les bétons à basse teneur en ciment, le rôle du ciment est néfaste.

III) Pour l'étude des propriétés thermomécaniques des bétons bauxite – SiC

Le carbure de silicium SiC, dans les bétons UBT, a une influence bénéfique sur les valeurs de module de rupture à chaud (HMOR), à 1400°C. Avec des mélanges, contenant un rapport de fines Al_2O_3/SiO_2 de 75/25, les valeurs de HMOR sont toujours croissantes jusqu'à SiC = 16%, mais lorsque le ratio Al_2O_3/SiO_2 = 25/75, cette amélioration n'est valable qu'avec des additions de SiC comprises entre 4 et 8%.

1) Le comportement des valeurs de MOR en fonction de la température va croissant jusqu'à 1000°C puis va décroissant au delà de 1000°C.
2) Les courbes HMOR vs T se décomposent en 3 zones de la température ambiante jusqu'à 600°C (zone élastique) de 600 à 1000°C (zone élasto-plastique) et au delà de 1000°C (zone visqueuse)

3) Les additions de SiC sont favorables pour améliorer la résistance aux chocs thermiques (TSR), mais sont maximales entre 4 et 8%.

4) Les effets positifs du SiC sont attribuables (a) au fait que SiC possède intrinsèquement un faible coefficient de conductibilité thermique élevé et une résistance mécanique élevée (b) que les cristaux de SiC sont principalement prismatiques, avec une résistance élevée aux contraintes thermiques (c) que les cristaux de SiC forment avec ceux de corindon et de mullite des réseaux entrelacés créant un fort renforcement de la structure.

IV) Pour l'étude du comportement rhéologique des bétons de haute alumine à ultra-basse teneur en ciment, sans et avec graphite.

1) Le comportement rhéologique de ces bétons est conforme à un fluide de type Bingham.

2) Avec des ultra-fines d'alumine et de silice, les propriétés rhéologiques s'améliorent en fonction d'une proportion croissante de microsilice. C'est la microsilice qui contrôle ces propriétés et permet d'obtenir de bonne qualité d'écoulement et des temps de travail adéquats.

3) Le rapport optimal ultra-fine d'alumine-microsilice ne doit pas dépasser 25/75. À 50/50, les propriétés rhéologiques chutent drastiquement.

4) La distribution granulométrique sur l'ensemble des tailles influence grandement la rhéologie de ces bétons. Il s'agit donc de choisir un paramètre d'Andreason, «q», relativement faible avec la quantité appropriée de microsilice.

5) Tant les paillettes de graphite naturel que les micro-boulettes extrudées de graphite ont une incidence négative sur les propriétés rhéologiques des bétons. L'influence des micro-boulettes est beaucoup moins marquée que celle du graphite naturel, même si la demande en eau est moindre (34% en moins), et ce aux différents taux de cisaillement. L'ordre de mérite des différents carbone est le suivant : pas de graphite mieux qu'avec micro-boulettes, mieux qu'avec paillettes de graphite.

6) Les performances supérieures, au point de vue rhéologique, obtenues en utilisant des micro-boulettes, résultent de leur meilleure hydrophilicité et dispersabilité, par rapport aux paillettes.

V) Pour l'étude du comportement rhéologique des bétons sans ciment, d'alumine-magnésie, sans et avec graphite.

1) Ces bétons, lorsque plus riche en microsilice, ont tendance à épaissir lors des mélanges et sont peu affectés par des additions de fines d'alumine.

2) Les additions de magnésie, inférieures à 10%, ont peu d'effet sur les propriétés rhéologiques, qui, sans carbone, sont portés à être fluidifiant en cisaillement. La quantité optimale de magnésie est comprise entre 6 et 10%. Les échantillons ont tous le comportement d'un fluide de type Bingham.

3) Toute addition de carbone (paillettes ou micro-boulettes) a un effet négatif sur les propriétés rhéologiques des bétons. Le comportement rhéologique des bétons avec micro-boulettes, est supérieur à celui des bétons avec paillettes, aux différents taux de cisaillement utilisés (même avec 30% de moins d'eau de gachâge). Ceci s'explique toujours par le degré d'hydrophilie et de dispersabilité plus élevé du graphite boulетté par rapport au graphite naturel.

4) Il a été possible de produire des bétons d'alumine avec 8% de magnésie et 4 à 6% de micro-boulettes de graphite, qui, grâce à leurs propriétés rhéologiques, seront pompables.

ABSTRACT

In this cooperative work between Ecole Polytechnique, Canada and Zhengzhou University, China initiated in 2000, the following subjects have been studied:

1) the rheological properties of the matrix part of bauxite-based castables;
2) the rheological properties of SiC containing bauxite-based castables;
3) the high temperature mechanical properties of the SiC containing bauxite-based castables;
4) the rheological behavior of low cement alumina-based castable with and without graphite addition;
5) the rheological behavior of zero cement alumina-based castable with and without MgO and /or graphite addition;

At first it was intended to optimize the factors affecting the rheological behaviour of a slurry containing up to 80% solids (such as super-fine silica and alumina addition, water/cement ratio, type and content of dispersants and powder particle-size), to use them in later work on the rheology of castables. The second and third subjects were tackled to understand the relationship between rheological behavior and high temperature properties and to optimize these properties for conventional castable used in iron making industry. The fourth and fifth subjects were initiated to contribute to the understanding of rheological properties of new alumina-based castables, containing magnesia and carbon.

The goals in each case are to identify the parameters which influence the most shear thinning or the shear thickening of mixes by measuring the rheological characteristics, torque

viscosity and yield stress (from rheometer) for self-flow and pumpable castables, and to assess the optimal conditions in the formulation of different mixes, including these newly developed carbon-containing castables, yet to be commercialized, at least those containing graphite.

In total, more than 200 different mixes have been prepared and their rheological behaviour studied. For this purpose, three methods have been used:

- Rotational viscometer —for study on rheology of matrix slurry;
- Flow table — for measurements of self-flowability of castables;
- IBB Rheometer —for study on rheology of castable mixes;

To further characterize the samples, conventional three point bending method has been adopted for measurements of HMOR, MOR-Temperatures and Stress-Strain relationship. Residual strength ratio after thermal shock cycling from 1200 ^{o}C to water-cooling and relationship of critical temperature difference vs. residual strength have been used for evaluating their thermal shock resistance.

Optimization of rheological behavior of the castables investigated has been achieved:

1) Controlling the total content and the ratio of ultra fine powders of microsilica and ultra fine alumina;
2) Controlling the particle size distribution (PSD);
3) Selecting suitable dispersants for a good flowability;
4) Optimizing cement content and water/cement ratio;
5) Optimizing content of fillers (SiC, MgO and/or extruded graphite pellets additions);

The whole research work has been divided into three parts, each constituting one chapter in this thesis (Chapter 4 to 6). It was conceived to allow the preparation of seven papers, five of which have been accepted and already published.

The obtained results are as follows:

I. For the study on the rheological behaviour of matrixes of bauxite-based castables

1) The components in the matrix investigated, such as super-fine silica and alumina addition, water/cement ratio, dispersants and bauxite particle-size, on viscosity, shear rate and shear stress of the slurries have effects with different degree. Ultra fine powder (microsilica and ultra fine alumina) and dispersants are found to be the main controlling factors.
2) Slurry viscosity is noticeably reduced with an increase of microsilica amount, but only slightly increased with higher ultra fine alumina amount. With either microsilica or ultra fine alumina or microsilica and ultra fine alumina additions, the rheological behavior of slurries exhibits the characteristics of a Bingham fluid.
3) Among the dispersants investigated, Castament FS-20 (polycarboxylateether) is the most effective in reducing viscosity, shear stress and yield stress of the slurries. Its optimum addition amount is 0.20 wt %.
4) With a decrease in the water/cement ratio, apparent viscosity and shear stress are slightly increased up to water/cement ratio close to 2 (19/9).

Based on these results, the range of optimum composition of the matrix with good rheological behavior has been obtained.

II. For the study on the rheological behavior of bauxite-based SiC-containing castables

1) Rheological behavior of the bauxite-based SiC containing castables with calcium aluminate cement and microsilica as bonding agents exhibits shear-thinning characteristics and follows Bingham flow pattern.

2) With variation of silicon carbide content from 0 to 16%, the rheological properties (torque, yield stress, variation of torque viscosity with testing time and flow resistance) of the castables are degraded; optimum SiC content in the castables is between 4 % to 8%.

3) In the bauxite-SiC castables with ultra low-cement content, the effect of cement on rheological behavior is very weak. But in the low-cement bauxite-SiC castables, the cement content has a significant negative influence on the rheological behavior.

III. For the study on the high temperature mechanical properties of bauxite-based SiC-containing castables

1) SiC addition in ULC bauxite-based castable specimens has remarkable effect in improving HMOR at 1400 °C. For specimens containing ultra fine Al_2O_3 / SiO_2 =75/25, HMOR increases with increase of SiC contents, whereas for specimens containing ultra fine Al_2O_3/SiO_2 = 25/75, the optimum SiC addition is between 4 ~ 8%.

2) MOR — T curves illustrate that MOR increases with temperature up to 800 °C or 1000 °C, after which MOR decreases significantly.

3) The stress-strain behavior of the specimens may be divided into three stages: elastic range from RT to 600°C; "plastic flow range" (600°C ~ 1000 °C) and "viscous flow" range (1000°C and above).

4) SiC addition is also very effective in improving TSR of castable specimens. With increase of SiC contents, significant increase in residual strength ratio is observed, with maximum values at 4 ~ 8% SiC addition.

5) The positive effects of SiC addition on HMOR and TSR of bauxite-based castables may be explained since: (a) SiC possesses lower thermal expansion, higher thermal conductivity and higher strength; (b) SiC crystals are mostly prismatic or elongated and are more resistant to thermal stresses; (c). SiC crystals interlaced into corundum-mullite structure creating a reinforcing effect.

IV. For the study on the rheological behavior of ultra-low cement alumina based castables with and without graphite

1) Rheological behavior of the ultra low-cement fused alumina castables follows Bingham flow pattern.

2) When ultra fine alumina and microsilica additions are used together in the castables, an increase in microsilica content does lead to a significant improvement of rheological properties of the castables. Microsilica is thought to be the controlling factor affecting the rheological properties and helps to achieve good flowability and to assure adequate working times..

3) When ultra fine alumina/microsilica ratio is higher than 50:50, rheological properties are degraded, showing higher torque and yield stress values. In order to achieve satisfactory

high- temperature properties, ultra fine alumina / microsilica ratio has to be close to 25/75 ratio.

4) PSD strongly affects rheological behavior of castables. For castables with a fixed lower q value, its rheological behavior can be considerably improved by adjusting microsilica content.

5) Both flake graphite and extruded graphite pellets additions have negative effects of different degrees on rheological properties of the castables. But the rheological behavior of extruded graphite pellets containing castables is much better than that of flake graphite containing castables under test condition of much lower water demand (water content reduced by water 34.4 wt %) at varying shear rates. In terms of rheology, the order of merit of carbon additions is: no graphite > EG pellets >> flake graphite.

6) The improvements of the rheological properties of the EG pellets containing castables are due to their better hydrophilic and dispersion properties, compared to flake graphite containing mixes.

7) With an increase of either flake graphite or EG pellet additions, and even with a corresponding increase in water content, rheological properties (torque and flow resistance at varying shear rates) of the castables are degraded, the former is much severer in degree.

V. For the rheology study on zero cement alumina-based MgO-containing castables with and without graphite

1) With an increase in content of microsilica addition in the MgO containing castables without any graphite, rheological properties show shear thinning characteristics, also their torque and yield stress, and their variations of torque viscosity and flow resistance with testing time, are remarkably improved. There is only little change in rheological behavior with variation of ultra fine alumina addition.
2) MgO addition at level lower than 10% in castables has little effects on rheological properties, showing shear thinning. Optimum MgO content is 6% to 10%. The rheological behavior of all samples tested follow Bingham flow pattern.
3) Graphite additions, either flake or extruded pellets, have negative effects with different degrees on rheological properties of the castables. The rheological behavior of extruded graphite pellets containing castables is much better than that of flake graphite containing castables even at a lower water demand (water content reduced by water 30 wt %) at varying shear rates. This can be explained by the inherent advantages of EG pellets over flake graphite, in terms of hydrophilic and dispersion properties
4) Based upon their measured rheological properties, the alumina-based castable with 8% MgO and 4 ~ 6% EG pellets should be suitable for pumping installation.

CONDENSÉ

Cette thèse a été entreprise à l'intérieur d'un projet de collaboration entre le CIREP de l'École Polytechnique de Montréal et l'Institut HTCI de l'Université de Zhengzhou. Le travail consistait à lancer des études sur le comportement rhéologique des bétons, utilisés dans l'industrie du fer et de l'acier. Il fut conçu à l'origine afin de travailler sur des bétons classiques de bauxite-carbure de silcium utilisés dans les poches tonneaux de fonte. En considérant des bétons familiers à l'Équipe de Zhengzhou, des bétons de bauxite-SiC, il a été prévu de mieux pouvoir cerner en quoi des variations de comportement rhéologique, lors des mélanges, pouvaient influencer les propriétés de ces bétons subséquemment. Evidemment, il convenait de déterminer les paramètres susceptibles d'influencer les propriétés rhéologiques des mélanges, c'est-à-dire leur viscosité apparente en fonction des taux de cisaillement et des temps de mélange. L'originalité de ce travail consistait donc à travailler sur des mélanges complets, avec 95% de charge solide. L'enjeu était de pouvoir mesurer la viscosité des tels mélanges.

L'intérêt de comprendre le comportement rhéologique des bétons s'est accru dans les années récentes en suivant les développements commerciaux pour les bétons auto-coulants et projetables et les nouvelles techniques d'installation de tous ces bétons. Comme le démontre clairement la revue bibliographique, objet du chapitre deux de cette thèse, l'évolution des bétons réfractaires est maintenant grandement tributaire des progrès dans les méthodes d'installation, et sur les possibilités d'obtenir des bétons pompables et projetables. Pour bien caractériser ces bétons, il convient de dépasser les mesures de viscosité apparente sur les

barbotines représentant la partie matrice d'un béton. La thèse a donc été centrée sur la mise en service d'un viscosimètre initialement conçu pour les bétons « portland». Cette thèse est essentiellement une thèse de type expérimental qui a pour but 1°) d'identifier les paramètres qui influencent la fluidisation ou l'épaississement des mélanges en fonction du degré de cisaillement et du temps de mélange de différentes familles de bétons 2°) d'évaluer les conditions optimales pour la formulation des mélanges incluant de nouveaux types de bétons contenant du carbone et notamment du graphite.

Les objectifs sont d'acquérir les connaissances nécessaires tant sur la préparation des graphites pour être utilisés dans les bétons contenant du carbone, que pour la caractérisation des propriétés rhéologiques des mélanges à très haute teneur en solides.

La stratégie, en partant avec les bétons de bauxite-SiC, a été d'étudier successivement les bétons à haute teneur en alumine à ultra basse teneur en ciment puis les bétons d'alumine-magnésie sans ciment, et d'étudier ces deux classes de bétons sans carbone d'abord puis avec addition de graphite : d'une part avec addition de paillettes de graphite naturel et d'autre part avec du graphite micro-bouletté par extrusion.

La réaction de cette thèse a été envisagée dès le début en fonction d'une thèse par articles. Ce document est donc constitué de sept articles dont 5 ont été publiés et deux à être soumis en date du 25 Avril 2004.

Ces articles sont intitulés:

- «Rheological behavior of the matrixes of bauxite-based castables» paru dans China's Refractories, Vol.12, No.3, pp.7-12, 2003.

- « Rheological behavior of bauxite-based, SiC-containing castables» paru dans China's Refractories, Vol.13, No.1, pp.3-9, 2004.
- «High temperature mechanical properties of bauxite-based SiC containing castables» à paraître dans Ceramics International publiée par Elservier, accepté le 25 Septembre 2003 pour publication en 2004 (manuscrit CERI 1603, 5 pages).
- «Rheological behavior of ultra-low cement alumina based castables» paru dans Interceram, Vol.53, No.1, pp.8-12, 2004.
- «Rheology of alumina-based graphite containing castables» accepté pour publication dans les comptes-rendus du "4th International Symposium on Advances in Refractories for the Metallurgical Industries" publiés par l'Institut Canadien des Mines et Métallurgie, à paraître en Août 2004.
- «Study on rheology of zero cement alumine-based MgO containing castables» à être soumis au "Journal of the Technical Association of Refractories", Japan, 2004.
- «Rheology study on alumina-MgO-graphite castables» à être soumis au "Journal of Refractories Applications and News", American Ceramic Society, USA, 2004.

La thèse a été divisée en sept chapitres. Dans le chapitre 1 d'introduction, on a précisé le but et les objectifs de ce travail (qui ont été cités précédemment). Dans le chapitre 2, une revue bibliographique concernant l'évolution générale du domaine des bétons réfractaires, a été effectuée en vue d'illustrer l'importance des nouvelles techniques d'installation, et notamment le pompage et la projection humide (le «shotcreting»). C'est parce que ces méthodes d'installation ont pris de l'importance que la poursuite du présent sujet, portant sur le comportement rhéologique des bétons, a trouvé sa pleine justification. La description détaillée des matières premières, de la préparation des échantillons et de leur composition respective ainsi que des techniques expérimentales utilisées, a fait l'objet du chapitre 3. Dans ce chapitre, en effet, sont révélés des détails pertinents qui ne figurent pas dans les articles publiés. Les trois chapitres suivants regroupent les sept articles. Le chapitre 4 est consacré aux 3 articles sur les bétons bauxitiques avec addition de carbure de silicium. Le chapitre 5 est consacré aux bétons à base d'alumine, à ultra basse teneur en ciment, sans et avec carbone (2 articles); le chapitre 6, lui, est consacré aux bétons à base d'alumine-magnésie, sans ciment, sans et avec carbone (2 articles). Dans le dernier chapitre, on retrouve les conclusions et les recommandations. Celles-ci sont reprises ci-après. Cette thèse aura au total permis de déterminer les paramètres qui influencent le comportement rhéologique des bétons et notamment leur aptitude à l'épaississement ou à la fluidification lors de leur cisaillement, en fonction des taux de cisaillement (et/ou de l'énergie de mélange imposée par le malaxeur) et des temps de mélange avant la prise. Cette étude aura permis de déterminer les grandeurs clés à mesurer pour déterminer à priori si un béton pourra être pompable et être projetable. Ces grandeurs sont la viscosité apparente des mélanges et leur limite d'écoulement. Cette étude aura aussi révélé des résultats inédits sur une nouvelle classe de bétons, celle des bétons contenant du graphite. Les principales étapes à bien contrôler pour ces bétons à base d'alumine, ayant une réfractivité élevée, sont :

1) la quantité totale de microsilice et le rapport microsilice/utra-fine d'alumine, avec des tailles de moins quatre microns;

2) la distribution granulométrique, avec un coefficient d'Andreasen approprié, pour l'application visée;
3) la nature et la quantité de dispersant requises pour une valeur initiale d'auto-écoulement donnée;
4) le rapport adéquat eau de gâchage/ciment, en cherchant à minimiser la quantité de ciment;
5) les proportions bien ajustées d'additifs : SiC, MgO, micro-boulettes de graphite et antioxydants selon les cas.

Tout ceci a été respecté lors de la préparation de quelques 200 mélanges, sur lesquels des études rhéologiques ont été réalisées, que l'on a subdivisé en 3 groupes : les bétons à base de bauxite chinoise, les bétons de haute alumine UTB, les bétns alumine-magnésie sans ciment.

Pour les bétons bauxitiques :

Deux études rhéologiques ont été effectuées, d'abord sur la partie matrice d'un béton bauxitique sans SiC, puis sur un béton bauxitique avec SiC, complet, c'est-à-dire avec matrice et agrégats. Ceci a permis de valider la démarche expérimentale et d'apprécier les possibilités du nouveau viscosimètre utilisé, le viscosimètre IBB.

Les deux études ont permis de préciser les proportions de microsilice et d'alumine ultra fine à utiliser, ainsi que le pourcentage de dispersant, un polycarboxylate-éther (Castamet FS-20) au niveau de 0.2% poids; la quantité optimale de SiC à ajouter (4 à 8%) pour obtenir des bétons auto-coulables, pompables et projetables. Les deux études ont permis de constater que ces bétons possèdent tous le comportement rhéologique d'un fluide de type Bingham, c'est-à-dire qu'ils sont des mélanges qui deviennent plus fluides sous l'effet d'efforts de cisaillement accrus et pour lesquels la viscosité apparente décroît. Ce sont des bétons avec une limite d'écoulement, c'est-à-dire qu'ils ne s'écoulent qu'à partir d'un certain effort seuil. Ces valeurs de viscosité apparente et d'écoulement seuil permettent alors de caractériser à priori les bétons pompables et les bétons projetables.

Pour les bétons alumineux à ultra basse teneur en ciment :

Les mêmes séries d'essais ont été effectuées sur les bétons à haute alumine, sans avoir à considérer la partie matrice. La partie innovante de ce travail a porté sur la caractérisation rhéologique des bétons avec addition de graphite naturel, sous forme de paillettes et sous forme de micro-boulettes extrudées.

Tant pour les bétons de cette catégorie, sans carbone, que pour les bétons avec graphite, l'addition de microsilice est essentielle, au niveau de 3% et le rapport alumine ultra-fine/microsilice doit être de 25/75.

L'addition de graphite rend les bétons plus visqueux et augmente la limite d'écoulement, mais tous les bétons conservent un comportement rhéologique d'un fluide de type Bingham. L'addition de paillettes de graphite naturel est à déconseiller. Les performances acceptables des micro-boulettes surtout par rapport au graphite en paillettes, viennent du fait que par le boulettage par extrusion, le graphite devient au total moins hydrophobe et plus facilement dispersable dans le mélange .

Pour les bétons alumineux sans ciment, avec addition de magnésie :

De nouveau, le rôle bénéfique de la microsilice sur les propriétés rhéologiques de cette classe de béton, a été bien mis en évidence. L'addition de microsilice réduit la viscosité apparente des mélanges et permet d'abaisser la limite d'écoulement. Encore une fois, et pour les mêmes raisons, l'usage des micro-boulettes est à privilégier et l'usage des paillettes de graphite n'est pas à recommander. Les mesures effectuées sur le viscosimètre IBB ont permis de bien quantifier les différences et permis de cerner les valeurs limites qui permettront de produire des bétons à base de carbone, pompables et projetables. Les résultats de cette thèse démontrent qu'avec un béton alumineux contenant jusqu'à 8% de magnésie, il sera possible d'ajouter de 4 à 6% de micro-boulettes de graphite et d'obtenir des propriétés rhéologiques acceptables, pendant au moins 40 minutes, tout en maintenant un comportement rhéologique de type Bingham.

<u>Conséquences</u>

Ces travaux nous ont permis de bien mesurer l'influence des 5 paramètres qui ont été identifiés : quantité de microsilice, rapport alumine/silice, distribution granulométrique, nature et quantité de dispersant, rapport eau/ciment, et ce, selon le type ou la classe de béton utilisé. Les résultats publiés révèlent les grandeurs critiques, de façon précise. Ces résultats sont aussi présentés dans le résumé qui précède. Pour les bétons bauxitiques, il est donc suggéré de limiter les additions de SiC de 4 à 8% poids, la quantité de ciment alumineux de 2 à 4% poids, avec un rapport alumine/silice de 1/3, total de 4% poids de fines, en suivant une distribution granulométrique continue de type Andreasen, avec un coefficient de 0.23. Pour les bétons alumineux sans ciment, il est préférable de limiter l'addition de magnésie (entre 6 et 10%) avec 3% de microsilice, et pour l'addition de graphite, de se limiter à 6% de micro-boulettes.

Ces derniers résultats sont très pertinents pour le développement futur des bétons avec graphite. Quant à l'utilité globale de la démarche, il est bon d'ajouter que les premiers résultats obtenus sur les bétons bauxitiques ont pu déjà être validés par un essai industriel, à la compagnie sidérurgique Capital Iron and Steel Co., à Pékin, Chine. En se basant sur les caractéristiques rhéologiques qui ont été présentées dans ce travail, il a été possible de préparer des bétons bauxitiques pour projeter dans une poche tonneau, pour le transport de la fonte, de 260 tonnes, en utilisant une pompe de Krosaki Harima Corporation. Il a été possible de garnir cette poche en maintenant une projection de matériaux de 4,5 tonnes à l'heure; 20 tonnes de béton ont été projetées. La durée de vie a été de 1200 coulées, une amélioration de 35% par rapport à la moyenne annuelle, pour l'année précédente. Ce résultat présente déjà, en soi, une justification satisfaisante pour l'ensemble des travaux effectués. Il est d'ores et déjà envisageable que d'autres essais industriels soient réalisés sur les bétons contenant du graphite. Il est clair qu'à la suite de cette thèse, la définition du comportement rhéologique des bétons va s'imposer comme un prérequis pour plusieurs études à venir.

Au total les points originaux de ce travail ont porté :

1. sur la détermination du comportement rhéologique des bétons a base d'alumine, sans ciment avec addition de graphite. Les résultats obtenus étaient des résultats inédits jusqu'au moment de leur publication.
2. sur la détermination des paramètres à ajuster pour obtenir des mélanges auto-coulables et pompables.

Ce travail permettra de poursuivre les développements requis pour l'obtention de bétons réfractaires à base de carbone, qui pourront servir dans de nombreuses applications, mais principalement dans l'industrie sidérurgique. Il s'agit d'une étape importante qui vient d'être franchie.

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AP	Apparent porosity
BD	Bulk density
CCS	Cold crush strength
CMOR	Cold modulus of rupture
EG	Extruded graphite
FG	Flake graphite
G	Flow resistance
H	Torque viscosity
HMOR	Hot modulus of rupture
HTCI	High temperature ceramics institute
LC	Low cement content
MOR-T	Modulus of rupture vs temperature
NC	Non-cement or zero cement
PLC	Permanent linear change
PSD	Particle size distribution
RT	Room temperature
SEM	Scanning electron microscopy
TSR	Thermal shock resistance
ULC	Ultra low cement content
ΔT	Critical temperature

CHAPTER 1. INTRODUCTION

The wet pumping and gunning installation methods for refractory castables are recent techniques which have been systematically developed in the last decade. Self-flowability and pumpability are two important characteristics and advantages to take into account. The pumping properties of castables are based on the rheological behavior, that is the flow and viscosity of the castables, in transportation hoses. Those two characteristics are key aspects to adapt castables to these new installation techniques.

In a joint program initiated between Ecole Polytechnique and Zhengzhou University in 2000, it was decided to tackle this new field of rheology for refractory castables. It was determined to start on a well-established system so bauxite-based castables, containing SiC were chosen as the most appropriate. This work led to the understanding of the effects of the matrix components of a castable. The roles of fine additive, of water/cement ratio and of dispersants were clearly revealed. The limitations on the percent amount of solids in the slurries were tested (up to 80% solids only). The impetus of this thesis was then set to select an appropriate method to measure rheology of castables, including both matrix and aggregates. So to study castable mixes with up to 95% solid content, appropriate rheometer, specifically designed to do so for concrete has to be used.

It was then decided to move on to test ultra low cement alumina-based castables, and to go to the newest and yet non-commercialized alumina-based containing graphite; then to zero cement alumina-based castables, without and with graphite.

Because the rheological behavior of castables is a key determinant for pumping castables, the aim of this work was to understand how the rheological properties of bauxite- and alumina-based refractory castables are influenced by:

- the nature of the aggregates (sintered bauxite and fused alumina) and the overall particle size distribution;
- the type of binders, dispersants (type and amount) and water demand for bauxite- and alumina-based LCC, ULCC and NCC;
- the type, nature, particle size and PSD of fillers (SiC, MgO, alumina, microsilica and ultra- fine alumina) in the matrixes;
- the type of carbon addition — flake graphite and extruded graphite pellets;

and to collect data on the shear stress vs. shear rate behavior of mixes to determine the main parameters which affect the flowability of castables.

The purpose of this work was set to define the appropriate characteristics to classify any castables mixes in terms of both self- flowability and pumpability. The objectives were to identify parameters which influence the shear thinning or the shear thickening of mixes by measuring the rheological characteristics, torque viscosity and yield stress (from rheometer) for self-flow and pumpable castables, and to assess the optimal conditions in the formulation of different mixes, including newly developed carbon-containing castables, yet to be commercialized, at least those containing graphite.

In total, more than 200 different mixes and specimens have been tested and some of them have been evaluated for their high temperature mechanical properties and thermal shock resistance. This thesis has been prepared to meet the requirements of a thesis resulting from the collection of seven scientific papers, five of them being already published.

Chapter 2 is composed of a literature review, presenting a brief description of the evolution of the materials, manufacturing and installation technology of castables. Since the most important aspect is installation, controlled in first part by the workability and flowability of the mixes, in paragraph 2.3 the main parameters and properties, which affect rheology, are reviewed. A selection of recently published papers on bauxite- and alumina-based self flow castables (rather than vibrating castables) containing SiC or magnesia, have been considered, in order to limit the number of papers to be reviewed. Also the latest results of studies and application on alumina-based castables containing carbon are analyzed.

In Chapter 3, raw materials used for the experiments, compositions of the castables studied, preparation of sample mixes and test methods for the experimental work of the thesis are described.

Chapter 4 is related to the results obtained on bauxite based, SiC containing castables, including the investigation on rheological properties of matrixes of bauxite-based castables and their high temperature mechanical properties (including high temperature strength properties at elevated temperatures, stress-strain relationship and thermal shock resistance). The chapter is composed of three papers:

Paper 1: "Rheological behaviour of the matrixes of bauxite-based castables" (Published in CHINA' S REFRACTORIES, Vol. 12, No. 3, 2003, 7~12). The first purpose of this paper is to evaluate rheological behavior of matrix of bauxite-based castables by studying the influences of ultra-fine powders (silica and alumina), water/cement ratio varying from 1 to 10, dispersant additions and particle size of bauxite fines, on apparent viscosity and shear rate/shear stress relationship, by using a rotational coaxial double cylinder viscometer. The second purpose of the work is to understand the rheological characteristics of castable matrix and optimize the matrix composition. The optimum conditions which have been defined, are then to be selected as the starting point of the second set of experiments to be considered next.

Paper 2: named "Rheological behavior of bauxite-based SiC-containing castables" (Published in CHINA' S REFRACTORIES, Vol. 13, NO. 1, 2004, 3 ~ 9). In this work, rheological behavior of low cement and ultra low cement bauxite-based SiC-containing castables have been studied, including the effects of SiC content and cement content on rheological properties of the castables. The results show that with an increase of SiC and cement content, rheological properties of the castables deteriorate. On the other hand, moderate amounts of SiC (4% ~ 8 %) and of calcium aluminate cement (2% ~ 4%) have very slight influence on rheological properties, (i.e. when the castables are sheared their torque and yield torque only slightly increase with the shearing speed). The rheological characteristics of the castables follow Bingham fluid and always show shear thinning behavior.

Paper 3: "High temperature mechanical properties of bauxite-based SiC-containing castables" (submitted and accepted by CERAMICS INTERNATIONAL in Sept., 2003 and to be printed in 2004). In this paper, high temperature strength properties (Hot MOR at 1300°C and 1400°C, MOR-Temperature curves up to 1400°C and stress-strain relationship from RT to 1200°C under 500N load) and thermal shock resistance (residual strength ratio and critical temperature difference ΔT) of ultra low cement bauxite-based SiC-containing castables with two different ultra fine alumina and microsilica ratios (Al_2O_3/SiO_2=25/75 and 75/25) have been investigated and the results have been discussed in correlation with microstructural characteristics. It is shown that SiC addition in the castables from 4% to 16% is beneficial to the mechanical and thermal shock resistant properties which are correlated with microstructrural characteristics.

In Chapter 5, the investigations on rheology of alumina-based refractory castable with ultra low cement bonding are introduced. Two kinds of castables, alumina castable and graphite-containing alumina-based castables were studied. Each set of results have been presented as a paper. The resulting two papers have been submitted and accepted, one has been already published, the other will soon be.

Paper 4: “Rheological behavior of ultra-low cement alumina based castables” (Published in INTERCERAM, Germany, Vol. 53, No. 1, 2004, 8 ~ 12). In this paper, rheological behavior of ultra-low cement fused alumina castables has been studied employing IBB rheometer V1.0 to measure torque (shear stress) as a function of shear rate. Effects of ultra fine powders (various alumina and microsilica ratio) and particle size distribution (PSD) with different q values (0.23 to 0.29) on rheological behavior have been investigated. Optimum ultra fine powder ratio (alumina/microsilica) and particle size distribution with good rheological properties are being defined.

Paper 5: “Rheology of alumina-based graphite-containing castables” (submitted and accepted for publication in the 4^{TH} International Symposium on Advances in Refractories for The Metallurgical Industries, Proceedings, Hamilton, Canada, in August, 2004, Published by Canadian Institute of Mining and Metallurgy, Materials, Canada). In this work, the rheological behavior of ultra-low cement alumina-based castables with addition of flake graphite and extruded graphite pellets has been investigated, using an IBB rheometer. Emphasis has been laid on the influence of the type and amount of carbon additions on rheological properties of alumina-based castables and the results are compared with corresponding alumina castable samples without any carbon addition. It is found that alumina-based castables with extruded graphite pellets have good rheological behavior and good flowability with lower water demand (< 6.3%) compared to alumina-based castables with addition of flake graphite and without any segregation during the shearing of castable.

As Chapter 4 was concerned with cement-containing castables and Chapter 5 concerned with ultra-low cement-containing castables, Chapter 6 is to cover the zero cement (no- cement) alumina-based castables with magnesia, and without and with graphite. The chapter is constituted of two papers:

Paper 6: "Study on rheology of zero cement alumina-based MgO-containing castables", (to be submitted to THE JOURNAL OF THE TECHNICAL ASSOSIATION OF REFRACTORIES, Japan, in May 20, 2004). In this work, the rheological properties of zero cement fused alumina-based MgO containing castables has been studied using the IBB rheometer to measure torque (shear stress) under varying shear rates. The values of flow resistance and torque viscosity are used to evaluate their rheological behavior. The effects of microsilica and MgO powder on rheological behavior of the alumina-based castables have been underscored.

Paper 7: "Rheology study on alumina-MgO-graphite castables", (to be submitted to REFRACTORIES APPLICATIONS AND NEWS, USA, in June 15, 2004). This paper presents the rheological behavior of zero cement alumina-based MgO- containing castables with addition of various content of flake graphite and extruded graphite pellets, investigated using the IBB rheometer. Their rheological results are compared with corresponding castable samples without any carbon addition. It is found that the alumina-based castable with 8% MgO and 4 ~ 6% extruded graphite pellets have satisfactory rheological behavior which follow Bingham fluid characteristics; they also show good flowability with lower water demand (<6.7%) and no segregation during the shearing of castable is observed.

The last chapter in this thesis, chapter 7, is devoted to the interpretation of the experimental results, and a comprehensive discussion, leading to general conclusions Considerations and suggestions for further study and development work on bauxite- and alumina-based castables for pumping installation are also presented. The original contributions made in this thesis are also underlined.

CHAPTER 2. LITERATURE REVIEW

2.1. INTRODUCTION

The preparation and application technologies of refractory castables, in the past two decades, have been marked by changes in labor productivity, installation efficiency, adaptability, energy saving, service performance and safety. At the same time, the application of castables has been vastly extended to high- temperature vessels in particular, leading to increased substitution of castables for refractory bricks, especially in metallurgical melting furnaces.

The fundamentals that have guided the development of the refractory castables include [1]:

◆ Rheology: for flowability and workability of solid-liquid suspension system, rheological characteristics, and the factors controlling rheological behavior.

◆ Colloid chemistry: for physicochemical phenomena of solid-liquid interface, the functions of surface-active agents and electrolytes and the control of sol-gel conversion.

◆ Powder technology: for preparation, characterization, particle size distribution and grain packing of powders.

◆ Thermodynamics: for control of phase composition and phase equilibrium, phase evolution during service and design of product formula composition.

The application technologies in refractory castables include:

■ Selection of materials: the composition and properties of the raw materials adjusted to service conditions.

■ Installation technologies: based on operation conditions, installation facilities and material characteristics.

■ Drying and firing technology: new techniques to improve baking efficiency and safety of installations.

■ Design of lining structure of vessels or furnaces: the design and optimization of structure of vessels or furnaces must be carried out according to service requirements and main properties of materials (e.g. thermal and mechanical properties, corrosion and penetration resistance etc.)

With the development of updated fabrication and installation techniques of refractory castables, the use of monolithic refractories has dramatically increased over the last several years. Today in Japan, the percentage of monolithic refractories in total refractories production is over 60%, (over 70% in Nippon Steel Co). It is expected that this trend will continue in the future [2].

The rapid development of monolithic refractories is closely linked with that of the installation methods as well as the R & D achievements in the materials themselves:

① Introduction of ultra-fine powders and progress of their dispersing technology

② Introduction of appropriate non-oxides leading to oxide and non-oxide (e.g. carbon, carbides, nitrides, Sialon and Alon etc.) composite materials.

③ Use of various additives with different roles

④ Adoption of advanced installation methods

This chapter is divided into three parts. In paragraph 2.2, a brief description of the evolution of the materials, manufacturing and installation technology of castables is provided. Since the most important aspect is installation, controlled in first part by the workability and flowability of the mixes, the main parameters and properties, which affect rheology, and some progress of studies on rheology of refractory castables are reviewed in paragraph 2.3. Finally in this paragraph, the recently published papers on SiC or magnesia containing bauxite- and alumina-based self-flow castables (rather than vibrating castables) have been considered. This of course limits the number of papers to be reviewed. Also the latest results of studies and application on alumina-based castables containing carbon are analyzed.

2.2. EVOLUTION OF MATERIALS, MANUFACTURING AND INSTALLING TECHNOLOGY OF CASTABLES

Toward the end of the 1970's, low cement and ultra low cement castables, began to emerge. By mid 1980's, refractory researchers strived for even better castables. As a result, no cement castables were introduced to the refractory market. In 1990's, based on previous low and ultra-low cement castables, researchers started to concentrate on trying to develop "user-friendly " self-flow castables. The novel castables have the sophisticated properties of low cement or ultra-low cement castables [3].

For the remarkable changes of castables from conventional to modern high performance, in terms of their performance, M. Rigaud [4] summarized the evolution of castable varieties, as illustrated in Fig. 2.1.

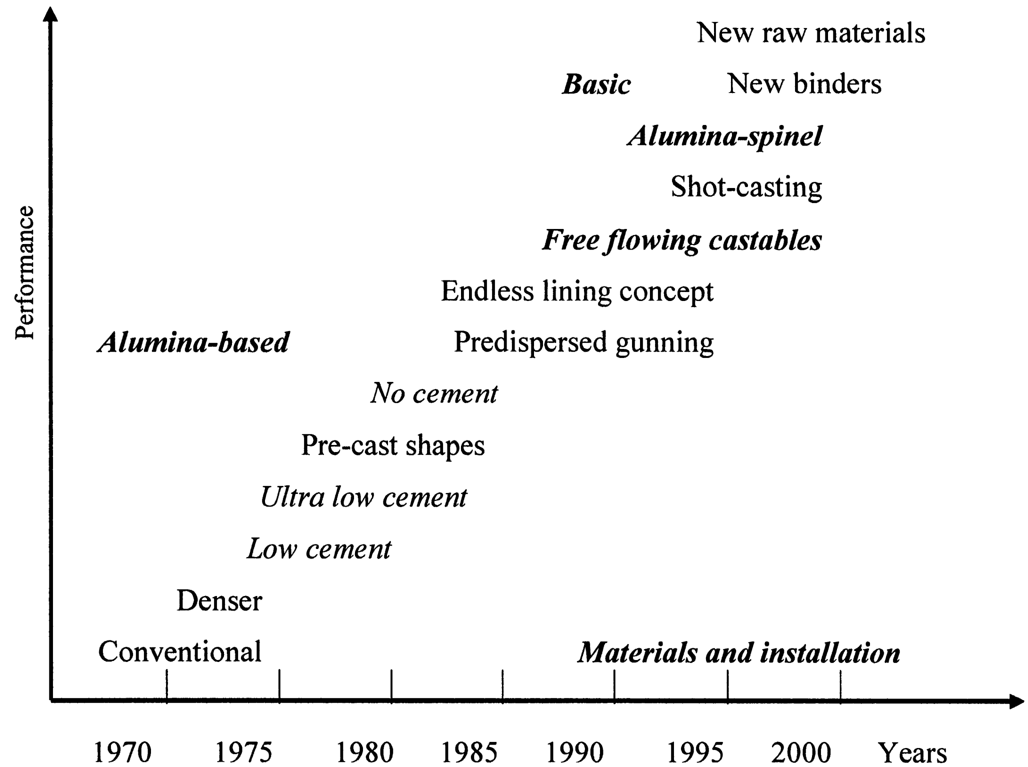

Fig. 2.1. Illustration of the material evolution of refractory castables over the last 30 years [4]

2.2.1 Raw materials and processing technology

Generally speaking, all raw materials, which are used to make refractory bricks, can be applied to prepare refractory castables. Formerly, the raw materials used for castables were mainly sintered natural raw materials, rejected materials from refractory brick production and recycled materials after use. As a result, the service temperatures were limited due to low performance of the monolithic refractories. Recently, synthesized and purified raw materials have been increasingly used. The changes in raw materials used are outlined as follows [5]:

Sintered natural raw materials, recycled materials

↓

Synthesized raw materials — *Homogenized type* | *Property optimized type* | *Converted type*

↓

↓

Purified raw materials — *Beneficiation* | *Addition of beneficial additives* | *Electro-fusion*

Because composition, properties and microstructure of raw materials used for castables are improved, the qualities of the castables are noticeably promoted. Therefore, the varieties of castables are significantly enlarged and its application scope is continually extended.

Obvious advancements have been also achieved in processing raw materials, resulting in improved shape of the coarse grains. Namely, the irregular shapes (pyramidal, columnar, acicular, flaky) of the grains are changed to nearly isometric or round shape, yielding a more favorable rheological behavior. To improve activity and sintering ability of the matrixes, the grain size of powder can be further minimized from normally <0.088mm (or <0.074mm) to <0.044mm, even smaller to micron size. The evolution is shown as follows [1]:

Less controlled grain size distribution, formulated mainly based on experience

↓

Three fractions of grain sizes for formula

↓

Multy-fractions (four to eight) of grain sizes

↓

Formulation based on particle size distribution (PSD) theories

2.2.2 Binders for castables

The properties of castables are closely related with the appropriate use of binders and additions. Binder systems can be differentiated into hydraulic, chemical or sintered [6]. The cement-containing bonding system described in ASTM C-401 [7] based on CaO content includes the no-cement, ultra low cement, low cement and high (regular) cement. There has been significant advancements in formulation and installation methods in the low to no-cement range. Included in these advancements are self-flowing, gunning, pumpable casting and wet shotcrete methods of installation. The chemical binders for castables can be classified into two types according to their chemical properties: inorganic and organic. The former can be in a solid state to be added and mixed with water, or in a liquid state to be used directly. The latter can be either used directly if liquid, or heated before used if solid. The following chemical bond systems are applicable in both acid and basic refractory systems.

1. Phosphoric acid;
2. Monoaluminum phosphate;
3. Alkali phosphate;
4. Alkali silicate
5. Silicic acid;
6. Sulfates

Only the magnesium phosphate system sets in ambient air and is insoluble in water. All other chemical bond systems require heat to set and become water insoluble [6].

Because most inorganic binders contain impurities which are harmful to high temperature performance of castables, the bonding mode is changed from hydraulic bonding (CA cement + water; ρ-Al_2O_3+ultra fine powders +water) to agglomeration bonding (CA+ ultra fine powders + water, Clay + water, Silica or Alumina Sol + electrolytes) or multiple bonding by hydration plus agglomeration.

Agglomeration bonding may be formed by coagulation of ultra-fine powders with water. The ultra-fine powders used in castables should have similar chemical properties with main materials or result in not much reduction of high temperature properties. The refractory castables with agglomeration bonding have the following merits:

- Low melting point phases resulting from the binders are minimized, thus high temperature performance of the castables is improved and they may be used under more rigorous conditions.
- Water demand for installation is decreased and hence porosity of the castables is reduced due to introduction of the ultra-fine powder. Overall performances such as workability, density and slag corrosion resistance have been enhanced.
- The castables have higher bonding strength at low, medium and high temperatures, because the ultra-fine powders have greater surface reactivity, as a result, the castables can be sintered at lower temperatures.

2.2.3 Additives for castables

The additives used in castables are for improvement on workability, physical and service properties of castables, and to prolong their service lifetime. They may be divided into the following types based on their function in castables [1]:

(1) To adjust workability (rheological characteristics), such as dispersants (water reducing agents), plasticizer, coagulator, deflocculant, fluidizing agents, etc.

(2) To adjust setting and hardening rates, such as setting accelerator agent, retarder, early strength enhancer, etc.

(3) To maintain the workability, such as preservative agent, acid inhibitor (swell reducing agent), anti-freezing agent etc.

(4) To adjust internal texture of materials, such as foamer, degassing agent, etc.

(5) To improve service performance, such as sintering aid, shrinkage inhibitor, expansion inhibitor, anti-explosion agent, antioxidant, etc.

To obtain high performance castables, the selection of suitable additives for various castables has become one of the key issues.

2.2.4 Workability of castables

The workability of castables was noticeably improved by introducing ultra fine powders, in particular microsilica, and by improving shape of grain and powder. In summary, the changes which occurred in workability of castables are as follows:

Poor thixotropy mixtures —vibration castables with higher water content

↓

Good thixotropy mixtures —vibration castables with lower water content

↓

Thixotropy free mixtures —self-flow castables, pumpable castables, shotcrete

Thixotropy free self-flow castables have the following characteristics:

♦ Vibration is not needed during placement. The flowing, degassing, leveling and compaction of the castables occur by gravity.

♦ Self-flow castables can be installed by pumping to location from considerably long distances (over 100 meters).

♦ Self-flow castables can be used to place and repair linings with complex structure, thin spacing or among densely-distributed anchors.

♦ Self-flow castables have less porosity, smaller and more uniform pores, and have commensurate properties.

2.2.5 Composition and varieties of castables

The compositions of refractory castables have been extended from acidic and neutral oxides (silica, semi-silica, clay, bauxites) to basic oxides (magnesia, magdoloma, magnesia-calcia-ferrite, magnesia-alumina, magnesia-chrome) and composites of oxide and non-oxide (carbon, carbide, nitride, sialon, alon, fibers etc). Typically, in terms of performance, the compositions of castables have been changed from clay, bauxites, high alumina (corundum), alumina-magnesia/spinel, and magnesia to composites of oxide and non-oxide [4].

2.2.6 Installation technology

Normally, two of the main requirements for refractories used in steelmaking and in related industries are high performance and easy installation. In order to meet these needs, placing techniques of refractory castables have progressed and are applied in different high temperature fields. Traditionally, use of moulds for installation was popular. Recently, it seems that time and labor saving, low cost placing, energy or resource saving and high efficiency of installation are more important in refractories industry. Therefore, based on self-flow castables, pumping and wet shotcreting installation are becoming more popular. Wet shotcreting method can be used not only for new lining installation but also for repairing residual linings after use.

The extension of installation technique for castables may be summarized from casting to pumping and wet shotcreting based on improvement of installation properties of materials. In other words, the change of installing methods is from installation in mould to formless installation, i.e.

Installation in mould — *Vibrating* / *Self-flowing* / *Pumping*

↓

Formless installation → *Wet shotcreting*

The development and application of wet shotcreting technique are based on the following advantages:

1) Good flexibility in top grain size of the mixes to be shot,

2) Directly forming lining configuration without need of mould,

3) Dust free, friendly operating environment in installation,

4) Minimum rebound of the shotcrete, reducing materials waste,

5) Keeping similarity in properties of castables compared with vibrating castables;

6) Higher installation efficiency and labor saving, low cost placing.

2.2.7 Installed properties of modern castables

Modern castables are self-flowing, pumpable and shotable castables developed since 1990's. Shotcreting (called similarly spraying or wet-gunning) has been presented in a number of papers in the recent years. Much of the presentations have been focused either on equipment, accelerators or research results on rheology of slurry of admixture matrix [3,8~14]. Research work on shotcrete has been fruitful in North America and Japan. The fact indicates that the shotcreting installation of self-flow castables as a current method shows a lot of superiority, not only for placing fresh castables in furnace or ladle linings, but also for repairing/maintaining furnace linings. Compared to common gunning, higher placement rates and higher densities can be achieved.

The castable pumping and shooting are a three-stage process that consists of mixing, transportation and spraying. A key issue is the fact that traditional measurements of flowability (ASTM or others) of castables cannot well-identify compositions that are appropriate for pumping [15]. Pumping and shooting castables must have more then good self-flow property for transportation, pumpbility and compactibility are to be defined.

2.2.7.1 Self-flow ability

Self-flow ability of castables is an important basic characteristic for shotcreting and pumping placement. The design of a self-flow castable must be based on the ability of the mix to be pumped through a hose/pipe system. Factors having an influence on self flowability include: specific gravity of material; particle shape and size distribution; character of powder and binder; accelerators and water addition etc. Self-flow castables has to have the following characteristics [16]:

- Good flowability under no action of external forces and no separation between grains and slurry.
- Proper flow from the hopper to fill each cylinder under negative pressure during the reverse piston stroke.
- Flow through extended lengths of pipe-hose without plugging, segregating or causing excessive pump pressure.
- Minimum or no dilatancy and tendency of segregation.

A test method ASTM C-1446 in 2001 [17] is now available to measure the working time and consistency or degree of self-flow of castables. But it is emphasized that this test method is not appropriate for determining the pumpability of castables because it cannot determine rheological properties of castable under shearing conditions.

2.2.7.2 Pumpability

Workability of pumping castables cannot be directly evaluated by self-flow ability of castables, but pumping should be based on self-flowing. In civil construction concrete, pumpability is defined as the concrete stability under pressure within an enclosed pipe. Another definition for pumpability is "workability" which is mobility under pressure. It is relatively easy to estimate workability or mobility by different standardized tests (such as slump). Pumpability has often been estimated by measuring power requirement or the actual pressure needs to effectively pump a certain castable mixture. Some researchers have tried to estimate the pumping rate graphically by considering the pump pressure, pumping transportation distance, pipeline diameter and castable slump. It seems appropriate to try to relate the slump or the rheological properties, which measure mobility, to pumpability. Beaupré [16] reported that ACI Committee 304 in 1982 has given recommendations regarding the slump limits for pumping. They recommend that concrete should possess a slump value from height direction between 50 mm to 150 mm, although properly proportioned flowing concrete with a slump higher than 180mm can also be pumped. Therefore, a most commonly used test in North America for civil construction concrete is the slump test measurement. The slump test (ASTM C-143-90a) [18] consists of filling a cone with concrete in a standard way; the cone is then lifted and the slump measured after the concrete has reached an equilibrium position (see Fig. 2.2).

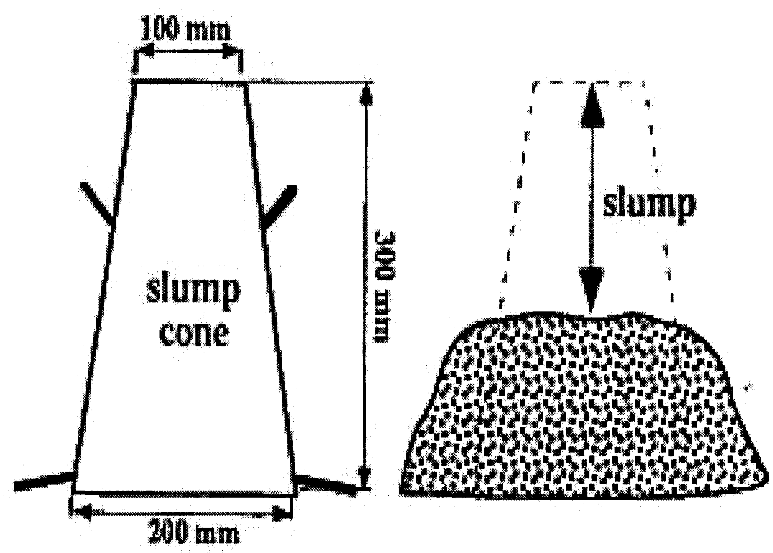

Fig. 2.2 Slump cone apparatus

Originally, the slump test was developed to measure the effect of water content on the workability of fresh concrete. The limits of its proper application correspond to slumps between 40mm and 180mm. In other words, this method is limited when pumping material is very stiff or very fluid.

There is yet no standard test method to evaluate pumpability so far.

H. Sumimura et al. [14] reported on an untraditional evaluation method, using an experimental apparatus shown in Fig. 2.3. The compositions of the castables tested in the apparatus are shown in Table 2.1. Two levels of water contents, 6.8 mass % and 7.1 mass % have been used. A castable mixture is filled in the model pipe with the discharge port closed by the shutter. It is held for three minutes under a load of 0.01MPa on the top of the charge. The discharge velocity (falling velocity) of the castables is measured when the shutter of discharge is opened. Also the piston type pump is used. Transfer tests of specimen A, B and C are carried out, and the discharge amount is measured under various pressures.

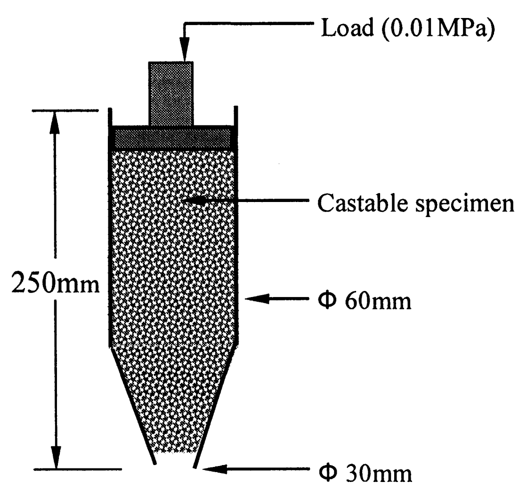

Fig. 2.3 Schematic figure of the dropping under load test

The results show that specimen A has a fastest falling velocity, and specimen C shows a lower falling velocity. Final evaluation for pumpability is that the test material with higher falling velocity and larger amount discharge even under lower pressure can be easily pumped. Comparing the two test methods, the former is simpler, but it is not appropriate for practical castables with dilatant rheological behavior. The drawback of the latter is that there is a tendency to separate easily between matrix and aggregates, and sometimes bridges formed between aggregates will cause a blockage due to smaller exit of the cone in the apparatus.

Table 2.1 Grain size distribution of tested castables

	A	B	C
> 1.0mm	++++	+++++	+++++
1.0 ~ 0.045mm	+++	+++	+++
< 0.045mm	++++	+++	+++
45 ~ 2μm / < 2μm	4.0	4.5	5.5

N. Fukami et al. [19] presented effect of additives on the pumpability of low cement castables. In their work, an apparatus with similar principle mentioned in above Figure 2.3 was use to describe pumpability of low cement castable. Pumpability is quantitatively evaluated from the discharge quantity and discharge pressure for the pumping test of the castables. The fluidity of the castables is evaluated from a V-funnel flow test and the homogeneity is evaluated from the Weibull parameter quantitatively.

In fact, pumpability can be affected by many factors. Operator and other influence factors [20], for instance, any change in mix compositions or in the materials characteristics would result in difference of pumpability. The variation of water content, PSD and environment conditions (temperature, moisture etc.) for installation could affect the workability of castables.

Although the flow consistency value obtained by a flow table test are used in many countries [14,21,22] as standard method for vibrating refractory castables, this method is unsuitable for pumping self-flow refractory castables with dilatant fluid characteristic.

2.2.7.3 Compactibility

When refractory castables are installed by pumping and shooting, moving speed of the castable depends mainly on the amount of compressed air used at the nozzle and their impact on the receiving surface area (or diameter of transportation pipeline) to produce the compaction effect. Thus compactibility should be seen as the efficiency of the method and/or of the equipment used to properly produce dense linings with respect to the workability of the fresh shotcrete. If the method and equipment for placement are capable of properly placing a dense material, then the compactibility of the castable is satisfactory [16]. A good compactibility will help to improve the density and the mechanical properties of castables.

2.2.7.4 Shootability

So far, shootability has yet no precise definition in the refractory industry field, it can be considered as the placing ability after adding at the nozzle setting-accelerator into concrete to be shot. Normally, flowability and pumpability of castables have to be considered for smooth transportation in pipeline. Other important parameters such as rebound and build-up thickness can also be an indication of quality after installation. Good shootability means no blockage in nozzle, less rebound and greater build-up thickness of castables in placement.

With pumped castables, compared to shotcrete, there are some differences in compositions and characteristics of materials, the main ones being the role of setting accelerator on high temperature properties. Pumping castable can be installed in moulds and without liquid accelerator at the nozzle's end. In this case, rebound and adhesion ability is not to be considered. But for shotcreted castables, these characteristics, which would decide quality of installation linings, are very important.

There is a permanent contradiction between pumpability and shootability [16]. When the pumpability is increased (for example, increasing its slump), its shootability is decreased (smaller build-up thickness); when the pumpability decreases, shootability increases. It is a challenge to find the optimum compromise between pumpability and shootability. When this optimum is reached, at least, a reduction of setting accelerator addition could be possible to minimize effects on high temperature properties of castables.

2.3. RHEOLOGY OF REFRACTORY CASTABLES.

2.3.1 Phenomenological aspects

Rheology is defined as the science of the deformation and flow of matter. The rheological behavior of a fluid characterizes its viscous behavior as a function of shear rate. But if no shearing force is acting on the fluid, its viscosity is only a natural property which indicate its fluidity. In this case, its rheology and viscosity are significantly different concepts.

For ceramic slurries and refractory castables, there are six time-independent rheological types in two different forms summarized by J. E. Funk [23,24]. Fig. 2.4-a shows them, as shear stress vs shear rate and Fig. 2.4-b shows them plotted as apparent viscosity vs shear rate.

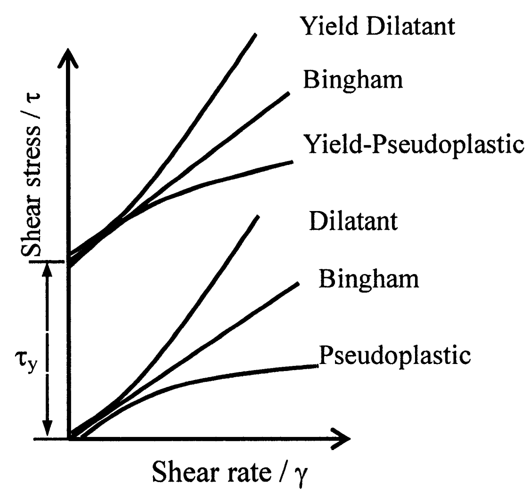

Fig. 2.4-a Six time-independent rheologies — shear stress versus shear rate

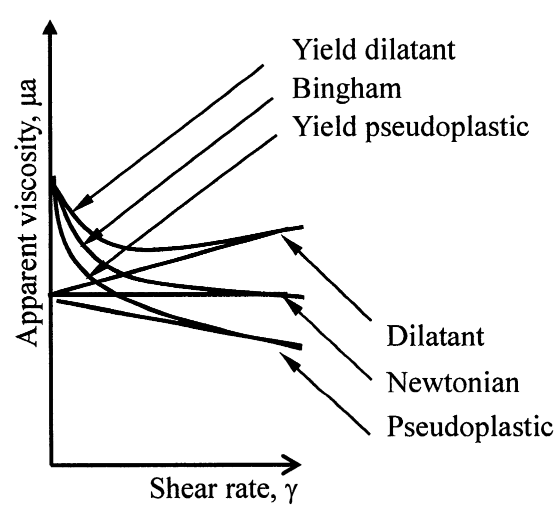

Fig. 2.4-b Six time-independent rheologies — apparent viscosity versus shear rate

The power law equations that correspond to the time –independent rheologies in Fig.4-a are:

(1) Yield-Dilatant: $\tau = \tau_y + K\gamma^n$ where $n > 1$; (2--2)

(2) Bingham (or Yield-Newtonian):

$$\tau = \tau_y + K_p\gamma^n \quad \text{where } n = 1; \qquad (2\text{--}3)$$

(3) Yield-Pseudoplastic: $\tau = \tau_y + K\gamma^n$ where $n < 1$; (2--4)

(4) Dilatant: $\tau = K\gamma^n$ where $n > 1$; (2--5)

(5) Newtonian: $\tau = \mu\gamma^n$ where $n = 1$; (2--6)

(6) Pseudoplastic: $\tau = K\gamma^n$ where $n < 1$; (2--7)

where: τ = shear stress, τ_y = yield stress, γ =shear rate,

K and n = empirical constants often referred to as the coefficient of rigidity and the flow index,

μ = Newtonian viscosity, K_p = plastic viscosity.

The Bingham equation (shown as equation 2--3) is commonly used to describe suspensions that exhibit yield-Newtonian behavior. Mathematically, yield-Newtonian or Bingham rheology differs from yield-pseudoplastic, but in practice, they are quite similar. A yield-pseudoplastic rheology may really be Bingham, but the rheogram may not have been measured at sufficiently high shear rates to detect the constant, high shear, Bingham viscosity.

Rheological behavior of castables covers relationships among shear stress, yield stress, shear rate, viscosity behavior under shearing and their variation with testing time before setting takes place. The rheological characterization of refractory castable is traditionally restricted to flow measurements, and only highly fluid castables are usually considered suitable for pumping [25]. Furthermore, the traditional techniques for rheological evaluation, which are based on flow measurements, cannot simulate the flow conditions of castables inside hoses.

One of important parameter of effects on rheology behavior is viscosity (η) which is the fundamental property that describes the flow or the behavior of a fluid. Viscosity and rheology are significantly different concepts [16,23]. The viscosity of a fluid is an indication of its fluidity, which can be defined as the relationship between the shear stress and shear rate.

When a sufficient shear stress is applied on the fluid, (or the shearing force per unit area), the fluid is deformed, at a certain rate, until the stress is relieved. The experimental determination of viscosity coefficient requires the measurement of shear stress under known conditions of shear rate and temperature. Apparent viscosity is simply the viscosity measured at one specific shear rate. If this value is constant at variable shear rates, the fluid is a Newtonian fluid, where its coefficient of viscosity, η, is the slope of the linear relationship [16,23] shown in Figure 2.5 and expressed by the following equation:

$$\text{Shear stress:} \quad \tau = \eta\gamma \qquad (2\text{--}8)$$

(η = Viscosity; γ = Velocity)

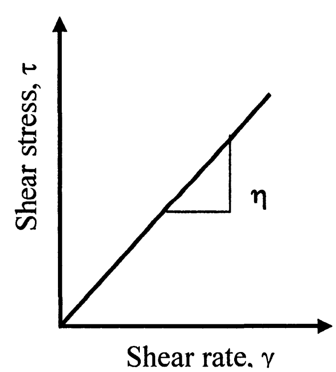

Figure 2.5 Determination of viscosity coefficient

For more complicated behavior, the observed rate of shear is not linearly proportional to the applied shear stress as shown in Figure 2.6.

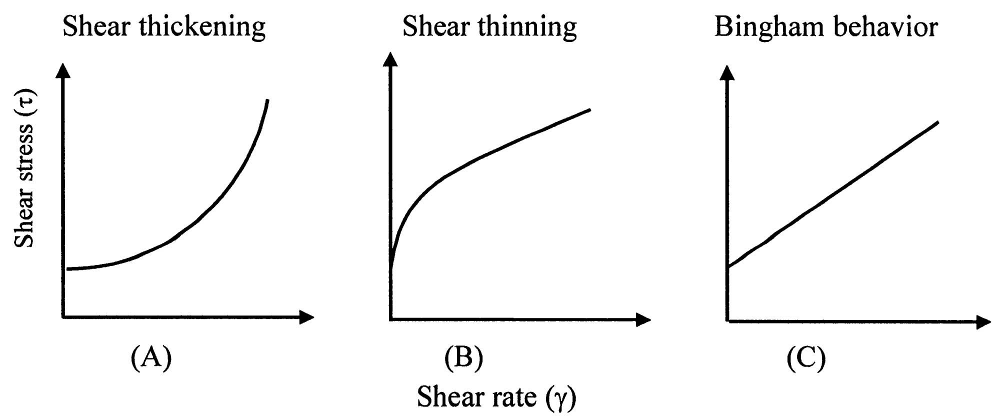

Fig 2.6 Non-linear flow curves and Bingham model ($\tau = \tau_y + \mu\gamma$)

For fluids (A) and (B), it means that minimum shear stress must be applied before the fluid starts to flow. The curve (A) shows a shear thickening fluid in which the viscosity is increased with an increase of the shear rate (slope increase). The curve (B) shows a shear thinning fluid in which the viscosity is decreased with an increase of the shear rate (slope decrease). For curve (c), when the yield value (τ_y) is overcome, the fluid starts flowing at a constant rate. This corresponds to a said Bingham fluid and the τ and γ relation can be expressed as:

$$\tau = \tau_y + \mu\gamma \tag{2--9}$$

where μ is the dynamic viscosity; γ is the shear rate. In this case, only two parameters are needed to fully describe the fluid flow behavior at shearing: the yield stress value and the dynamic viscosity.

2.3.2 Other practical aspects

2.3.2.1 Effects of dispersion on rheological behavior

The castable matrix behaves in a manner similar to particulate suspension. Therefore, dispersion of particles in the matrix is an essential requirement to obtain castables associating high flowability with low water content. Furthermore, dispersion inhibits the formation of agglomerates that can hinder optimum particle packing and affect castable final mechanical strength. Matrix dispersion can be accomplished by increasing the surface charges of particles in slurry. An effective method for this is to use suitable dispersant. The study on dispersion of microsilica-containing zero-cement high-alumina castables by A. R. Studart et al. [26] indicate that based on the zeta potential data obtained, citric acid can be an effective dispersant for the alumina- microsilica binary matrix, because it provides the same electric charge sign on the particles surface of both powder at the usual pH range of aluminous castables. But in another investigation [27] on dispersants for high-alumina castables without microsilica and zero cement, A. R. Studart et al. found that zeta-potential data alone is not an appropriate parameter to select dispersants for alumina-based zero-cement castables and suspensions when high solids loadings are concerned. Salt-neutralized poly-acrylic acid leads to suspensions with superior viscosity and yield stress when compared with those dispersed with citric acid. The shear rate and shear stress curves obtained shows that suspensions dispersed with sodium polyacrylate and citric acid exhibit pseudo-plastic behavior. The viscosity of suspensions containing citric acid is lower then that obtained with sodium polyacrylate.

In order to determine the conditions for simultaneous dispersion in the alumina-SiC system, I. R. Oliveira et al. [28] studied the deflocculation for this system. Results show that simultaneous dispersion of the binary system must take several parameters into account, in order to achieve well-dispersed and homogeneous system. When mixed to form a binary system, unary systems of alumina and SiC dispersed preferably with the same dispersants, provide a high surface charge of the same sign with sodium polyacrylate or polyethyleneimine. Both dispersants are used in concentrations that were previously obtained from deflocculation curves. For these systems, the potential ratio between two powders is positive and close to one.

G. Oprea et al. [29] reported rheology studies on binding systems for self-flow castables. In order to find a correlation between the rheology of a binding system water suspensions and the flow characteristics of castables, measurements of viscosity, pH and flow have been analyzed for different combinations of plasticizers, accelerators and retarders in binding systems with three and four ceramic components, including the hydraulic binder. Results show that when used together, the phosphatic additive and organic additive prove to be effective dispersants for ULCC with low purity microsilica, allowing to obtain self flow values of up to 90 % at 6.0 % water, but small variations in their concentration produce important modifications of viscosity levels. It appears that the main effect in reducing the viscosity is due to the presence of the phosphatic additive. Most of the mixes do not show a direct correlation between viscosity and pH.

2.3.2.2 Effects of ultra fine powders on rheological behavior

Now, microsilica and ultra fine alumina are mostly used in LC, ULC and NC castables. The beneficial effect of microsilica is related to its submicron particle size and globular morphology. By using a suitable dispersing agent, microsilica particles can be dispersed uniformly in the castables. When microsilica is added to the castable, it fills even the smallest pores and displaces the water present in the voids. Thus the flocculated structure in the castable matrix is disrupted and the water in fillers is released, resulting in lower water demand and better dispersion of particles in the matrix.

S. Odanaka et al. [30] reported the effect of alumina fine powder and microsilica addition on the fluidity of castables by measuring their apparent viscosity. Calcined alumina (> 99.2 % Al_2O_3) and microsilica (86.4~96.4% SiO_2) as raw materials have been tested. Results show that effects of addition of alumina and microsilica on fluidity of castables depend on their chemical composition and PSD. Microsilica with higher impurity content, especially alkaline impurity, gives higher viscosity. Finer alumina gives higher flow values. B. Myrhe [31] studied influence of super fines on properties of high alumina castables. Results show that both microsilica and alumina have the effect of fillers. The microsilica is however significantly more effective, resulting in potentially lower porosity for the final refractory. The microsilica with high purity gives the highest flow values of castables.

2.3.2.3 Effects of particle size distribution (PSD) on rheological behavior

The 3 main particle packing equations used to describe castables are known as Andreassen or Furnas or Dinger-Funk equations:

Andreassen equation: $CPFT / 100 = (D/D_L)^q$ (2--10)

Furnas equation: $CPFT / 100 = (r^{\log D} - r^{\log Ds}) / (r^{\log L} - r^{\log Ds})$ (2--11)

Dinger-Funk equation: $CPFT / 100 = (D^q - Ds^q) / (D_L^q - Ds^q)$ (2--12)

where, D — particle size; D_L — largest size; D_S — smallest size;

q — PSD coefficient; r — ratio of particles between two adjacent sieves;

CPFT — cumulative volume percent;

In practice, the equation mostly widely applied is the Andreassen's equation.

R. G. Pileggi et al. [32] reported study on rheology and particle-size distribution of pumpable refractory castables. In their work, white fused alumina aggregates (>100μm) 55 ~ 69 %, was used with calcined alumina matrix (<100μm) 45 ~ 31 %, and a q values varying from 0.21 to 0.31. Results indicate that castables with similar flow values may display distinct rheological behavior ranging from pseudoplastic to dilatant, Therefore, rheological characterization is necessary to design pumpable castables. In the particle-size range studied, q = 0.26 is the most suitable composition for pumpable castables. This coefficient defines the optimum balance between superficial and mass-related forces in the system, resulting in pseudoplastic castables that are less influenced by volume restrictions. They also show that LC castables composed with a large fraction of fine matrix particles (q = 0.21) do combine high fluidity with low water consumption. However, increased matrix content deteriorated all the other properties evaluated. The mixing effort and of what increased while the drying speed decreased. In contrast, the excess of aggregates in the q = 0.31 composition inhibits its fluidity, which prevents its application for pumping and shotcreting. High performance behavior is achieved by the q = 0.26 composition because of its intermediate contents of matrix and aggregates.

The results of investigation [33] on PSD on rheological properties of high alumina multi-functional castables show that PSD remarkably affects the rheological behavior, determining the techniques recommended for use during installation. PSD curves based on Andreasen's packing model with q = 0.26 allows for the production of high performance castables. These castables can be installed using various methods (ramming, vibrating and self-flowing), simply by changing the water content used during their preparation.

Result of study on flow control of low cement self flow castables by V. Jones et al. [34] shows that granulometry is obviously of extreme importance and increasing the number of the coarsest grades and widening the overall particle size range of a castable formulation increased the flow and workability of the original formulation. Particle shape of the raw materials is also observed to have an effect on the rheology.

2.3.2.4 Effects of water addition and cement on rheological behavior

The water content for castables has been dramatically changed through the years, from high water amount (10~20%) to low water content (4~7%). Accompanying this change, rheological properties and flowability of castables have nevertheless noticeably improved and the installation technologies have progressed.

The strength of refractory castables is improved when a minimum amount of water is used. For pumping into forms, this minimum water is dependent on the flow and consistency requirements needed to fill the form. For installation with no vibration, water level needed should be slightly higher than that for castables with vibration. In shotcreting, the material has to be safely pumped to long distances plus pass through a nozzle in which the air pressure effectively breaks up the column of material in the hose. If the castable is too dry or too wet, it is difficult to obtain a good installation body. Generally, the optimum water demand is the proper self-flow level in which the castables properly fill, and aggregates in castables are covered very well by matrix slurry.

With the introduction of ultra-fine powders and the change in bonding system, castables have attained higher packing density because water in the voids of the mixes is replaced by ultra-fine powders, leading to lower water addition. In mixing, particles have a natural tendency to agglomerate. Efficient breakdown of agglomerates directly influences the rheological behavior of suspensions. R. G. Pileggi et al. [35] reported how adding water for mixing in sequence affects the rheology of castables. To prevent agglomeration after mixing and to produce stable, low viscosity suspensions, particles must be contacted with dispersing agents. They show [35] that castable mixing is significantly influenced by PSD and the water addition method used. Two-step water addition leads to high torque values at the turning point, resulting in maximum mixing efficiency and greater castable fluidity. In contrast, although the torque values at the turning point using one-step water addition are low, this procedure fails to display good efficiency in breaking up agglomerates, which is reflected in low flow values. Results demonstrate that castables require a minimum mixing energy to reach maximum flow value combining high mixing efficiency (short mixing time), which is obtained with a two step water addition.

The water/cement ratio (W/C) in mixture is certainly an important parameter with respect to the setting and flowing characteristics of castables. Castable with low W/C ratio would possess very high flow resistance and a very high torque viscosity, and low flowability. As the W/C ratio of castables is reduced, the suitable water-reducer must be used to produce required workable properties.

Normally, water demand for hydration of cement in castables is closely related to the amount of cement added. In cement–microsilica bonding system (low cement or ultra-low cement bonded), cement and microsilica simultaneously contribute to the viscosity. Microsilica contributes to bonding by agglomeration, whereas cement provides bonding through hydration. The hydration mechanism of cement in this system may occur as follows [36]:

$$CA + H \rightarrow CAH_{10} + AH_3 + CH \qquad (2\text{—}13)$$

$$\downarrow$$

$$C_2AH_8 + AH_3 + CH \rightarrow CH + uf\text{-}SiO_2 \qquad (2\text{—}14)$$

$$\downarrow$$

$$C_3AH_6 + AH_3 + CH \qquad (2\text{—}15)$$

$$\text{C–S–H hydrates}$$

Due to hydration of cement, very small particles of amorphous Ca $(OH)_2$ are formed which would react with highly reactive microsilica particles on their surfaces to form calcium silicates hydrates (C-S-H). As a result, hydrated C_3AH_6 and AH_3 phases decrease in quantity. Therefore, in the ultra low cement bonded system, there is no need to increase substantially the water amount for the above reaction. It follows that the effect of cement on rheological behavior is rather weak. However, if cement content in castable is over the range of ultra-low cement castables, the excess cement leads to an increase in viscosity [37] and degradation in rheological properties of the castables, and hence more water has to be added for hydration reaction of the cement. This may probably explain why the effect of cement on rheological behavior in the ultra low cement castables is less than that in the low cement castables.

2.3.2.5 Effects of additives on rheological behavior

To maintain good workability and obtain good installation quality, the use of additives (such as setting accelerator agent, retarder, early strength enhancer, anti-freezing agent etc) is an important know-how. The paper of A. E. C. Peres et al. [38], named "rheological approach on selection of additives for wet gunning castables", presents a comparative study among sodium silicate, sodium alumina and an organic additive. Rheological properties of a commercial 70% alumina wet gunning castable were evaluated by a special rheometer, and its matrix was studies by viscosimetry techniques. This methodology makes possible the selection of the best type of additive and its minimal level to modify the castable consistency and also to understand the mechanism of rheology changes. The conclusions are that inorganic additives, such as sodium silicate and sodium aluminate, present instability as coagulants because they allow the concrete to recover high free flow with time. The minimum amounts to use are of the order of 0.4% for sodium silicate and 0.6% of sodium aluminate. Organic additives are more appropriate for wet gunning, showing a strong coagulation of the concrete for a minimum amount of 0.6% in weight. The mechanism of reduction of the flow occurs by coagulation and not directly from the acceleration of the hydration reactions of cement. On the contrary, the two inorganic additives tested present a gradual slow increase of the yield stress values. From a previous study [38], the efficiency and the coagulation stability of additives can be classified in the following order: organic > sodium silicate > sodium aluminate.

During mixing of castables, there is an initial period of very rapid hydration followed by a dormant period during which very little reaction takes place. This period is responsible for the usual 2~3 hours period known as placing time. Once setting has occurred, the physical properties of the castables can be measured. In the dormant period after mixing, the characteristics and properties of castables will change slowly. The flow resistance may increase gradually until setting. So, the setting characteristics (as well as rheological behavior) of castables has to be adjusted by adding additives according to various requirements and conditions, such as environment's temperature; humidity; properties and types of fine powders and ultra-fine powders used (mostly micro-silica and /or micro-alumina); properties, types and content of cement etc. The selection of additives should be considered when the castable composition is designed.

2.3.2.6. Rheology of castable matrixes

With the development of refractory castables with high performance, the rheology of the castables as basic research becomes a new and hot scientific topic. The research works on rheological principle started on the matrix slurry of castables first. Though rheological behavior of matrix in castables cannot be equal to that of castable mixes, the rheological behavior of castables is greatly affected and controlled by its matrix.

A. R. Studart et al. [39] reported evaluation on rheology of castable matrix. The surface chemistry of raw materials possessing particles <100 μm, and specific surface area >1m^2

plays a major role in castable dispersion. The matrix rheology is assessed for variations in both dispersant concentration and pH value in suspensions holding the same ratio of fine alumina particles to water as commonly found in castables. According to this assessment, the concentration of solids used is 58 vol. % (~ 84 wt %). Rheological measurements are carried out with the help of a digital rheometer (model LVDV-III). Matrix rheological analysis is accomplished at different PHs and citric acid content through measurement of shear stress in a sweep cycle of continuously increasing and decreasing shear rate of 2.5 to 50 s^{-1}. The date are averaged over 20 s of measurement at a given shear rate. The viscosity data measured at a shear rate of 50 s^{-1} is considered. Their conclusions indicate that the rheology of high solids loading suspensions is significantly influenced by the pH and citric acid content. In spite of the elevated surface potential at high pH values, alumina particles covered with citric acid molecules can form weak agglomerates in the basic region, and show that castable self-flow ability depends on an appropriate control of viscosity; yield stress and non-Newtonian characteristics of the matrix.

J. B. Baldo et al. [40] investigated effect of the matrix (< 150 mesh particles) mass fraction and the deflocculant type (phosphate and polyacrylate based) on the development of a self-flowing low cement (2 wt%) high alumina refractory concrete. The water addition ranged from 4 to 5.5 %. It was found that apparently the optimum matrix mass fraction for self-flowability is around 39 wt%. The use of phosphate based deflocculant renders a less viscous matrix with high fluidity indexes and the deflocculant content equal or less than 0.1 wt% irrespective of level of mixing water.

Jiang et al. [10] studied rheology of matrix of high alumina castables, using revolving cylinder viscometer. The viscosity and the shear rate of the matrix slurry were measured. The influence of water addition, type and content of cements, grain size of high alumina powder on the viscosity and the shear rate of the slurry is studied. It is found that cement content in the slurry has a great influence on the fluidity; also the smaller the grain size of powder is, the better the fluidity is.

Y. Song et al. [11] studied rheological behavior of alumina-spinel-cement suspension by means of a rotary viscometer. It is found that with the optimum addition of CA cement and the ratio of superfine powder (< 2μm) to fine powder (< 0.088 mm) being 0.43, adding the optimum addition of the polyphosphate dispersant, the matrix of alumina-spinel castable shows a good rheological behavior.

W. D. Resende [41] presented the rheological properties of alumina-carbon suspension with 30 and 75 % solid concentrations respectively. The correlation between viscosity, zeta potential, and adsorption measurements is examined. It was found that Vanisperse CB, an anionic dispersant, has shown the highest zeta potential values and is not only able to decrease the viscosity of carbon black suspensions but also for alumina carbon system. The viscosity reduction of the suspension may be related to the existence of electrical repulsive forces arisen from adsorption of deflocculant onto particle surfaces.

2.3.2.7 Experimental methods to characterize rheology

I. Measurement of self-flow value of castables

This is a simple test that consists of filling cone with standard dimensions on a flat surface (flow table). The cone is filled with the castable to be tested. Then the cone is lifted, allowing the castable to flow freely, as a result of gravity. Flow parameter then is defined as the percentage increase in the spread diameter relative to the initial cone base diameter.

In works of A. R. Studart et al. [33], the rheological behavior of castables prepared with distinct q values (from Andersen's packing model) is evaluated by measuring the self-flow value obtained according to the procedure adapted from ASTM standard C-1445 [17]. They considered that the self-flow behavior is usually characterized by self-flow values of 80 to 110%. The castable that require vibration during installation, on the other hand, may present self-flow values 30 to 80%. Compositions presenting self-flow values of < 30% are usually installed using more energetic techniques, such as ramming. Castables exhibiting self-flow values >110% may be susceptible to segregation, because the matrix density may not be sufficiently high to prevent the sedimentation of coarse particles. It is assumed that the distance separating aggregates is the main influencing factor for castable flowability. But this method cannot indicates pumpability of castables.

II. Evaluation on rheology of matrix slurries by revolving cylinder viscometer

Authors of the references [10,11] used revolving inner cylinder viscometer for measuring and evaluating the rheology of matrix of high alumina castables. Its working principle is: the slurry sample is placed into a cup, inner cylinder is used as a rotor and a motor drives this inner cylinder, in the slurry, at different revolving rates. From the measurements of the torque and the shear rate of the slurry, the torque viscosity is calculated, to evaluate the rheological behavior of slurry.

III. Evaluation on rheology of castable by rheometer

R. G. Pileggi et al. [25] introduced a newly developed digital rheometer. The rheometer is assembled from a planetary mixer, a round-based bowl with a capacity for 10Kg castable, an electric engine and control system. The DC engine has a variable rotation speed range of 0~3000 rpm, which allows precise control during measurements. The rotary speed can be controlled by adjusting the feeding voltage, which is linearly proportional to the speed. The equipment controls the rotation speed (shearing) of the paddle used to mix the castable and to measure the force (torque). Hence, the rheometer enables simulation of different application technique for castables and provides adequate evaluation of their rheological behavior. In their work, the mixing process is evaluated using the rheometer to detect torque variations as a function of time during the addition of water. The torque values obtained indicate the castable resistance to mixing and shearing [39].

In CIREP at Ecole Polytechnique, and HTCI of Zhengzhou University, an IBB rheometer [16] developed by the UBC has proficiently been used to measure rheological parameters of the castable samples for evaluating their rheological behavior.

This rheometer can monitor the applied torque, control the speed of castable shearing and record all the rheological parameters with high accuracy. It consists of a sample bowl and 3/4 HP motor that drives an H-shape impeller with a planetary remove. The imposed torque is gradually increased with different speeds during the test. By recording torque data at different impeller speeds it is possible to calculate yield stress and shear stress values which reflect the rheological behavior of castables. It can be expressed in terms of two parameters by the following equation:

$$T = G + HN \qquad (2\text{—}16)$$

Where T is the value of torque applied to the impeller (Nm); G is the flow resistance (Nm); H is the torque viscosity (Nm.s), and N is the impeller angular speed (rev/s).

The torque stress is a function of shear rate; the flow resistance (G) is related to the yield stress, and the torque viscosity is related to the plastic viscosity; Although the G and H values are instrument-dependent properties, by means of proper calibration, they can be related to the yield stress τ_y (Pa) or to the plastic viscosity μ (Pa.s), which are two fundamental rheological material properties.

2.4. ALUMINA-BASED SELF-FLOW CASTABLES

Self-flow castables were first introduced to North American market in the 1990's. Their applications in the steel industry include electric furnace deltas and spouts, ladles, tundishes, reheat furnaces and a variety of areas in blast furnaces.

The important aspects of obtaining high quality lining by way of self-flow castables are: 1) proper self-flow ability of castables and 2) proper dispersant and accelerator and its minimal addition for the requirements of material properties.

In theory, most refractory materials for preparing vibration castables can be used for manufacture of self-flow castables. But in fact, it is difficult to prepare some light-weight self-flow castables (bulk density < 1.0 g / cm^3) because specific gravity of the raw materials is smaller, and too much pores in raw materials are filled in by micro-powders. Depending on requirement of application at different service conditions, many different refractory raw materials, used successfully for LC, ULC and NC castables, have been used for preparing self-flow castables. To optimize self-flowing characteristics, optimization of PSD is necessary, in particular to prevent segregation. If the castable is pumped over longer distances, the material must remain fluid, with proper setting time to break up inside the shotcrete nozzle, so that better spraying action is achieved.

The raw materials used include: clays, bauxites, andalusite, mullite and fused or sintered aluminas. Many self-flowing castables made from those raw materials have been widely used in various high temperature industries, with different installing methods. In the section to follow, a review of pertinent papers, already published on the subject, is to be presented.

2.4.1 Bauxite- and alumina-based SiC-containing self-flow castables

Many papers have been published on the alumina-based, SiC-containing castables and on the bauxite-SiC system, mainly in China [42~47]. In this chapter only two other papers are to be mentioned specifically, since they refer to self-flow castables characterization.

S. Joseph et al. [48] work is on self-flowing alumina-silica-(SiC) castables. They used bauxite and tabular alumina as main raw materials to make SiC-containing castables with water addition of 4.25 ~ 6.0 %. Self-flow values of the castables reached 150 ~ 210mm. These products are similar in design to current low-cement castables but can be easily installed by pouring into place from a mixer or pumped/poured using regular concrete pumps. Compared to vibrated regular low cement castables, their properties are similar. The pourable flow characteristics at low water content have increased the speed and ease of castable`s placement. Various installations in the steel, cement, alumina, and incinerator industries are detailed including mixing-pumping techniques, and time-cost savings are considered.

The other paper is by Wang et al. [49] who have developed Al_2O_3-(SiO_2-)SiC-C self-flow castables which have been successfully used for BF troughs. The main raw materials used for the castables are: bauxites (Al_2O_3 > 86%), fused bauxite-based alumina, fused brown alumina. CA cement and microsilica are used as binders. Determination of flowability was done using a flow table test without shock or vibration. Those castables show much better properties then that of vibrating castables. Table 2.2 shows their chemical composition and properties. To obtain a high performance, the key was to use the appropriate PSD, and more effective dispersant and ultra-fine powders were optimized.

In these two papers, there was no work to characterize the rheology and viscosity of the castables. We did use their results to design our own bauxite-SiC system castable, and present our results in chapter IV.

2.4.2 Alumina- and alumina-spinel self-flow castables

H. S. Kang et al. [50] have presented their development of such self-flowing castables for application in the cement industry. Results show that superfine particles and water addition of castables have a great influence on fluidity.

Two alumina-based self-flow castables, bonded from low cement and ultra-low cement, are developed, using a proprietary accelerator and commercially available equipment, reported by B. Myhre et al. [51]. The castables have the composition with aggregate top size 4 mm, and contain 84 % fused alumina. Those alumina based castables were said to respond well to the accelerator and to be readily pumpable and thus suitable for shotcreting.

Table 2.2 Chemical composition and properties of the Al_2O_3-(SiO_2-)SiC-C self-flow castables

		1	2
Chemical Composition, %	Al_2O_3 SiC + C	≥ 65 ≥ 14	≥ 73 ≥ 18
B.D. g / cm^3	110°C, 24h 1500°C, 3h	≥ 2.80 ≥ 2.75	≥ 2.85 ≥ 2.83
P.L.C. %	1100°C, 3h 1500°C, 3h	-0.5~+0.5 0~+0.6	+0.05 0.17
C.M.O.R. MPa	110°C, 24h 1100°C, 3h 1500°C, 3h	≥ 4.0 ≥ 4.0 ≥ 6.0	≥ 7.5 ≥ 8.0 ≥ 10.0
C.C.S. MPa	110°C, 24h 1100°C, 3h 1500°C, 3h	≥ 15.0 ≥ 20.0 ≥ 30.0	≥ 25.0 ≥ 35.0 ≥ 50.0
HMOR, MPa	1450°C, 1h	≥ 1.50	≥ 3.0
Water addition, %	5.2 ~6.0		
Flow value, mm	180 ~230		

H. Nakashima [52] et al. presented applications of self-flow type castables in NKK. Results indicate that with the vibration installation type castables as a basis, new self flow castables having properties equal or even superior to the conventional ones can be developed and applied to various linings in NKK's works. The application has covered a blast furnace runner, reheating furnace skid pipes, tundish lining and ladle bottom lining, and permitted confirmation of such favourable effects as labor saving of installation and reduction of cost per charge.

In a Ph.D thesis of K. Sankaranarayanane [53], properties of alumina self-flow castables (SFC) with ultra-low cement as binder were studied. Tabular alumina aggregate, fine matrix (-325 mesh reactive alumina, calcined alumina, microsilica) and additives (deflocculant, accelerator and retarder) were taken as the three major constituents of the self-flow castable used in the investigation. Results show that self-flow property was influenced more by the microsilica, deflocculant, retarder and accelerator whereas flow-decay time was affected by temperature, retarder, accelerator and microsilica. Self-flow values decreased with increasing polypropylene fiber (PPF) content and length. High viscosity of fine matrix of SFC with increasing PPF addition indicates higher resistance to self-flow. Study on effect of PSD indicated that increasing the amount of coarse grain decreased the apparent porosity, MOR and notched-beam fracture surface energy. An increase of the coarse grain amount decreased R_{th} while increased R^{IIII} and R_{st}.

Y. Song [54] presented flowability of self-flowing alumina-spinel castable by means of flow table. The study is focused on the influence of the particle distribution in aggregate portion and the ratio of aggregate to powder on the flowability. It is found that when the distribution of aggregate portion is close to the Anderassen curve with the q = 0.22, the castable has good properties and 214mm self-flow value.

A paper named 'The matrix advantage system, a new approach to low moisture LC self-levelling alumina and alumina spinel castables' by G. W. Kriechbaum et al. [55] reported that new fine aluminas, fine spinels and CA cement have been developed as part of the 'Matrix Advantage System' (MAS). Microsilica-free low cement tabular alumina castable and tabular alumina-spinel castable with low water content were studied. The MAS has allowed the development of low moisture self-levelling castables with controlled but flexible placement properties in a wide temperature range. The water demand, to achieve self-levelling flow performance of such castables, with a 5% cement addition, is 4.0 ~ 4.7 %. The major physical and mechanical properties of these castables and the corrosion behavior of selected castables against basic slag have been tested. The placement, setting and flow properties in a environment temperatures between 7 ~ 35°C are demonstrated. These castables have remarkable volume-stability in high temperatures, even at 1650°C a firing shrinkage of only 0.4 to 0.6 % has been observed. Again it is proven that the addition of alumina-rich spinel significantly increases the HMOR at 1500°C. Strength values over 20 MPa up to 33 MPa can be easily achieved. It has been demonstrated that the new matrix system is also suitable for vibration castables.

In China [56], corundum self-flow castables with Al_2O_3 content from 80 ~ 90 % have been successfully applied for petrochemical and metallurgical industry; among them Al_2O_3-Cr_2O_3 self-flow castables have been used for EAF roofs, porous plug and incinerator linings. The use of alumina-magnesia castables for steel ladles has become popular, in the last decade, in response to the increased severity of operational conditions and to the demand for improved steel's quality. The alumina-spinel self-flow castables with Al_2O_3+MgO content of 80~90 % have been successfully used for ladle lining, lance (for pre-treating molten iron) and reheating furnace lining. Their chemical composition and properties are shown in Table 2.3.

Table 2.3 Chemical composition and properties of alumina-based self-flow castables

		A	AM	AK
Chemical composition, %		$Al_2O_3 \geq 90$	$Al_2O_3+MgO \geq 94$	$Al_2O_3+Cr_2O_3 \geq 94$
B.D , g / cm^3	110°C, 24h	≥ 3.00	≥ 2.90	≥ 3.10
	1500°C, 3h	≥ 3.10	-	≥ 3.15
C.C.S. MPa	110°C, 24h	≥ 50.0	≥ 60.0	≥ 50.0
	1500°C, 3h	≥ 80.0	-	≥ 90.0
C.M.O.R MPa	110°C, 24h	≥ 10.0	≥ 10.0	≥ 10.0
	1500°C, 3h	≥ 12.0	-	≥ 14.0

On the basis of an alumina-magnesia castable, R. Masumoto [57] set up to develop a alumina-magnesia shotcreting material for ladle side wall, (except slag line) and bottom. The alumina-magnesia castable currently used for ladles formed the basis for the review of particle size constitution and the effective use of ultra-fine powder. Their two goals were: to develop a shotcreting material formulation to achieve an installation texture comparable to that obtained by vibrating castable for the side wall of the ladle, and to find a quick-setting agent that would enable thick patching of the vertical wall to 200 mm thickness.

N. Fukami [58] presented alumina-MgO castables with 88 % to 92 % Al_2O_3 content and 5 % to 9 % MgO content, as shotcrete, to be used for big capacity steel ladles. The shotcreting was applied not only for an existing repair of castable lining, but also for the placement of an initial lining.

2.4.3 Alumina-based carbon-containing castables

Carbon–bonded refractories have been developed in the past two decades, to be used in steel making and continuous casting processes. Alumina-carbon high performance castables have good prospects in applications as functional monolithic refractories. Now, the functional refractories for continuous casting process of steel making, such as long nozzle, submerged entry nozzles and stopper-monoblock, are a class of high performance refractories mostly composed of carbon-bonded alumina-based materials with higher carbon contents (15~30 wt%); they are formed by isostatic pressure apparatus and may not be considered as true castables. To meet the requirements of applications, they possess superior performance to resist the harsh service conditions (such as erosion by molten steel over 1600°C, corrosion by slag, thermal shock of temperature difference between air and molten melts). However, the application of these refractories with higher carbon content results in a problem, i.e. the carbon in refractories at high temperatures can be dissolved into molten steel, resulting in an increase of carbon in steel and hence affecting steel quality, especially, when they are used for producing high quality steel (such as ultra-low carbon steel or cleaning type steel). Therefore, the need for low carbon containing refractories offers an opportunity for development of carbon containing castables and application in continuous casting process.

As a carbon source for shaped refractories, there are many choices. It has been proven that best choice is flake graphite, when compared to other carbon sources. The benefits of graphite are due to its high purity, perfect crystallization, good oxidation resistance, and superior slag corrosion resistance. Therefore, the flake graphite has been used as the prime carbon form for refractory bricks.

However, carbon-containing castables with good properties, are yet to become commercial, even if the potential market demands are great. Unfortunately, the development of carbon-containing castables is still very slow. This is mainly due to technical difficulties. For example, incorporating the natural graphite into castables is quite difficult owing to its poor wettability, which does lead to dispersion and flowability problems, and thus higher water demand has been needed for casting. The large difference in density between the graphite and refractory oxide raw materials can lead to segregation. The high porosity caused by higher water demand and lower strength caused by poor bonding between graphite and refractory oxides at elevated temperatures are also important issues to be solved. According to H. Teranishi et al. [59] flowability of MgO-carbon castable, using flake or grain graphite, coke, pitch, carbon black as carbon sources and controlling the castable flowability as the same level as an Al_2O_3-MgO castable, the water demand, at 5% carbon level, can vary from more than 18% with flake graphite down to 10% with amorphous graphite and 7~6% with other sources of carbons (coke, pitch, carbon black). The later is close to that of a conventional Al_2O_3-MgO castable. They also found that a MgO castable with a combination of 5% addition of pitch and carbon black, had a lifetime at the slag line more than twice that of an Al_2O_3-MgO castable. The properties of the MgO castable used are shown in Table 2.4.

S. Zhang et al. [60] summarized that aqueous wettability and dispersion properties of graphite could be improved by coating technique with materials such as carbides (SiC) and oxides (Al_2O_3, TiO_2, SiO_2, MgO and ZrO_2). The MgO-C castable containing 4% graphite coated by SiC has 174mm of vibrated flow value with 6.5 % water amount. Whereas for similar vibrated flow value (170mm), the water demand for untreated graphite castable is 11%.

Table 2.4 Properties of MgO castables

Chemical composition, %	MgO 90 %; C 5 %	
Apparent porosity, %	110°C, 24h	15.3
Bulk density, g/cm3	110°C, 24h 1500°C, 3h	2.71 2.65
Cold crushing strength, MPa	110°C, 24h 1500°C, 3h	28.3 25.4
Permanent linear change, %	1500°C, 3h	+0.64

Sakamoto et al. [61] prepared SiC-coated graphite by a high-speed impact method. SiC powder (5μm) can stick on the surface of the graphite (100~150μm) by using impact force, compress force and friction force during the mixing. Observation by SEM show that very fine SiC powders cover the surface of graphite and the shape of the graphite becomes spherical. The improvement of SiC coated graphite on dispersibility was confirmed by measurement on slurry Zeta-potential and flowability on Al_2O_3-SiC- C castables. This method for producing coated graphite is low in cost, but coating can be removed during abrasion mixing because of only physical binding between SiC and graphite. MgO-SiO_2-C castable developed with 85% MgO, 7% SiO_2 and 7% carbon have good strength at 20 °C to 1600°C. Its slag corrosion resistance is comparable to resin-bonded MgO-graphite brick used for ladle slag zone.

Facing those technical difficulties, for the preparation of graphite-containing castables, M.

Rigaud et al. [62~65] have carried out much work on developing extruded graphite (EG) pellets to modify the flake graphite properties for application in alumina-based and magnesia-based castables. Many investigations on physical and mechanical properties as well as oxidation resistance and corrosion resistance of carbon containing castables have also been done and are still ongoing.

The extruded graphite pellets are found to possess the following advantages [65]:

1. Increasing specific gravity of flake graphite by agglomerating or packaging graphite flakes and refractory oxide together;

2. Upgrading the pellets in terms of densification pore size and oxidation resistance by incorporating suitable anti-oxidant and oxide fillers inside the pellets;

3. Improving hydrophilic properties of flake graphite and reducing its segregation during the castable mixing;

4. Decreasing total water demand for mixing castables and reducing porosity of the carbon containing castable.

As an example the EG pellets have been used for preparation of MgO-carbon castables with 6% carbon content. The main material for the castables is magnesia sintered, having five size fractions of 6.7~3.35mm, 3.35~1.18mm, 1.18~0.3mm and 0.3~0.05mm, and ball-mill fines <0.074mm. Microsilica, metallic silicon and silicon carbide as binder and anti-oxidants are used for the forsterite-bonded castables and active alumina, metallic aluminium and boron carbide are selected for spinel-bonded castables. It was proven that the extruded graphite pellets is efficient in reducing water addition (<6% water content and >175mm flow value) and pore size and amount, increasing bulk density, CMOR (>10Mpa after treated at 110°C, 24h and 1500°C, 3h respectively), thermal shock and oxidation resistance properties of castables.

Reviewing overall, the advancements and varieties in materials for castables, progresses in preparation and installation technologies of castables and their property improvements are a long-time work. It should aim at high quality castables with lower cost and also at extending applications to high temperature critical areas or parts working under severe conditions, such as slag line and impact pad of ladle lining and delta area of EAF roof. For these purposes, alumina-based and magnesia-based castables with much improved properties are still needed. The improvements in rheological properties of castables for pumping or shooting installation constitute, at this point, fundamental research, which should be meaningful for developing new castables.

CHAPTER 3. EXPERIMENTAL PROCUDURE

This chapter introduces raw materials used for the experiments, compositions of the castables studied, preparation of sample mixes and test methods for the experimental work of the thesis.

3.1 Raw Materials

The raw materials used for the tests include fused alumina, fused MgO, SiC, flake graphite and extruded graphite pellet additions, ultra fine alumina, microsilica (Elkem 971U) and calcium aluminate cement (Secar 71). Their chemical compositions and particle size are shown in Table 3.1.

Graphite (EG) pellets used are prepared in CIREP by extrusion method, using mixes of natural flake graphite (C $\geq$ 97.0%, < 0.074mm), refractory oxide and anti-oxidants with a suitable organic binder. After heat treatment, the binder is pyrolized to form carbon bonding in the pellets. Then, surface of the pellets is treated with an organic agent to improve their hydrophilic properties. Subsequently, they are crushed and sieved into different particle sizes. Complete description of the pellets preparation is to be found in reference [60].

Table 3.1 Compositions and particle size of raw materials

Raw Materials	Composition and Particle Size
Fused alumina	$Al_2O_3 \geq 98.5\%$, 5 ~ 0.088mm, < 0.074mm, D50 = 42.05μm < 0.044mm, D50 = 22.91μm
Bauxite	$Al_2O_3 \geq 85\%$, < 0.074mm, D50 = 38.5μm, < 0.044mm, D50 = 14.1μm
Fused magnesia	MgO ≥ 85%, < 0.074mm, D50 = 40.2μm, < 0.044mm, D50 = 20.0μm
SiC	SiC ≥ 96 %, < 0.074mm
Flake graphite	C ≥ 96.0%, < 0.088mm
Extruded graphite pellets	C ≥ 85.0%, 1~4mm, Φ = 1mm
CA cement (Secar 71)	Al_2O_3 69.0~72.2 %, CaO 27.0~30.0%, D50 =12.0μm
Microsilica (Elkem 971U)	$SiO_2 \geq 97.0\%$, < 1.2μm, D50=0.51μm
Ultra-fine alumina	$Al_2O_3 \geq 98.5$ %, < 4.0μm, D50 =1.8μm

3.2 Composition and Preparation of the Mixes

According to different purposes, various formulations and compositions have been designed as slurries and castables.

1) Preparation of slurry samples

The slurry samples are for studying rheology of matrixes of castables. The purpose is to understand the effects of various factors, such as ultra-fine powders (silica and alumina), water/cement ratio, dispersant additions and bauxite fines ratio etc, on rheological behavior. Totally, 8 groups （108 samples） of the samples have been prepared and their details of formulations are shown in chapter 4.

2) Preparation of castable mixes and specimens

Using the test results obtained with the previous slurry samples, matrixes with ratio 1:1 of two particle sizes (< 0.074mm and < 0.044mm) of SiC, fused alumina and fused MgO as fillers have been considered for the different castable mixes. Ratio of coarse grains and matrix is 60~65/40~35. According to Andreasen's particle size distribution (PSD) pattern, an approximate q value of 0.29 is used for most of the castable samples (except the tests on effects of PSD on rheological behavior). 12 groups （40 samples） of alumina-based castable samples, respectively containing different contents and/or types of ultra fine powders, cement, SiC, MgO, graphite and various PSD etc., have been prepared for the rheological experiments, and 10 groups (61 samples) of two series of bauxite-based castable specimens with different ratio of ultra fine powders (alumina/silica) have been made for studying high temperature mechanical properties. The sizes of the castable specimens are 40×40×160mm and 25×25×125mm. Their details of formulations and compositions are shown in the chapters 4 to 6.

According to composition design, a 10kg castable mix for each rheological test is uniformly mixed and then well blended adding water in two-steps, for rheological measurements. Water content for each group of tests has been controlled at different levels.

3.3 Test Methods

(1) Method for measurement of flowability — Flow table

Flowability is represented by flow value which is measured using a flow table. Measuring consists of filling cone with standard dimensions on a flat surface (flow table). The cone is filled with castable which is prepared by first dry mixing for 3 minutes, then wet mixing for further 3 minutes. When the cone is lifted, the castable flows freely as consequence of gravity. Flow parameter then is defined as the percentage increase in the spread diameter relative to the initial cone base diameter.

(2) Method for studying rheology of matrix slurry samples — rotational viscometer

The rotational coaxial double cylinder viscometer (NXS-11A model), as schematically shown in Figure 3.1, is used for measurement of viscosity of matrix slurry which contains 18 ~ 20 wt% liquid and ~80% solid powders (< 0.074mm). The shear stress at varying shear rate can be measured. The viscosity curve (η vs D) and flow curve (τ vs D) are then used to appreciate their rheological behavior. The work principle of the viscometer is as follows: the slurry sample is placed into the annular gap between the outer cylinder and the rotor. A motor drives the inner cylinder with different speeds. A viscosity related torque, caused by the resistance of the sample to shearing, acts on the inner cylinder. This torque deflects a measuring spring placed between the motor and the inner cylinder. The size of the spring twist correlates linearly with the torque. The spring deflection shows up as an indication on the scale.

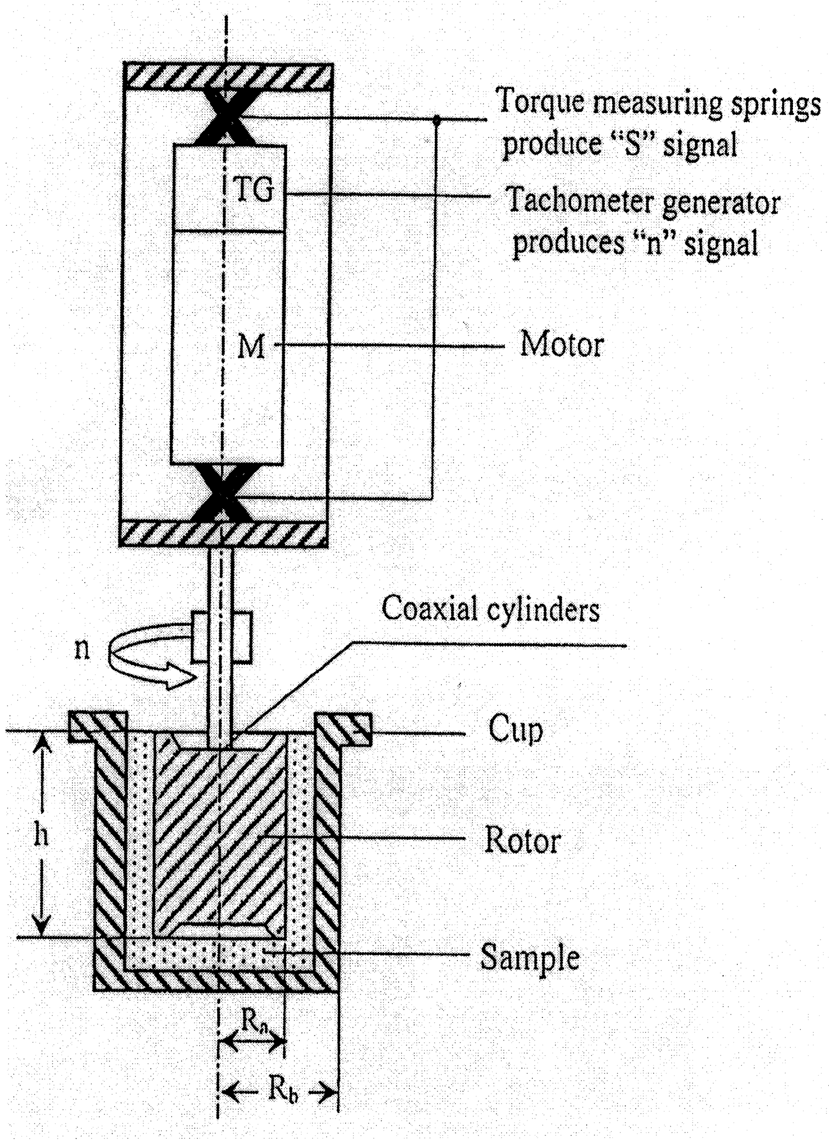

Fig. 3.1 A schematic set-up of the rotary viscometer

The viscosity and shear stress for evaluation of the rheological properties of sluuries can be calculated by the following formula:

$$\eta = \tau / D \qquad (3\text{—}1)$$

$$\tau = \ T/ 2\pi R_1^2 h \qquad (3\text{—}2)$$

$$D = \ 2\omega R_2^2 / (R_2^2 - R_1^2) \qquad (3\text{—}3)$$

$$= \ [(\pi/15) \cdot R_2^2 / (R_2^2 - R_1^2] \cdot n = K \cdot n$$

Where η= viscosity (Pa·s), τ = shear stress (Pa), D = shear rate (sec.-1), R_1 = radius of the inner cylinder-rotor, h = height of the inner cylinder, R_2 = radius of the outer cylinder-rotor, T = torque, ω = $2\pi n/60$, angular velocity (radians/sec.), n = rotor speed, shear rate factor that depends only on the radius of the sample cup and the rotor.

There are 5 measuring systems consisting of 5 sets of inner and outer cylinders respectively for a wide measuring range from 0.28×10^{-2} to 18000 Pa.s. Each has 15 velocity gears, yielding 15 varying D –values. Increasing the velocity of the rotor, taking down each reading (α) on the scale at each D, and the shear stress can be obtained by

$$\tau = Z \cdot \alpha \qquad (3\text{—}4)$$

where Z is a cylinder geometry dependent constant, available with the instrument, and α is the scale reading. By the τ-D curve, flow pattern is assessed.

A typical flow curve, as shown in Figure 3.2, indicates the yield stress τ_y corresponds to the intercept of the extended straight line to τ axis, and the dynamic viscosity η, which is the slope of the linear part. It is consider that fluid with low τ_y and η values, exhabits good flowability.

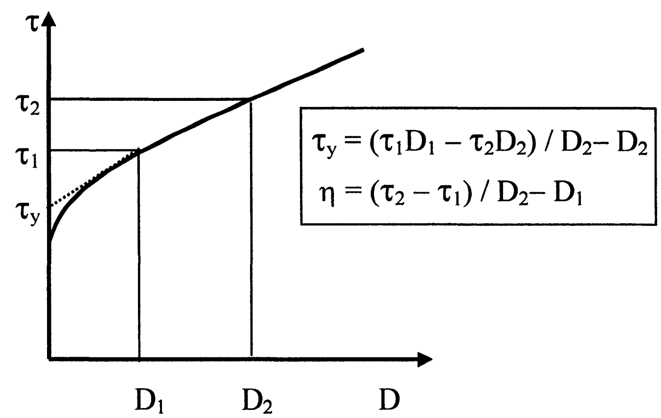

Figure 3.2 Yield stress and dynamic viscosity for plastic flow pattern

(3) Method for studying rheology of castable samples — Rheometer

An IBB rheometer (shown in Fig. 3.3) developed at UBC [16], has been used extensively to measure rheological parameters of the castable samples.

This rheometer can monitor the applied torque, control the shearing rate of refractory castable and record all the rheological parameters with high accuracy. It consists of a sample bowl and 3/4 HP motor that drives an H-shape impeller with a planetary remove. The imposed torque is gradually increased with different speeds during the test. By recording torque data at different impeller speeds it is possible to calculate yield stress and shear stress values which reflect the rheological properties of refractory castables. It can be expressed in terms of two parameters by the following equation:

$$T = G + HN \qquad (3\text{—}5)$$

Where T is the value of torque applied to the impeller (Nm); G is the flow resistance (Nm); H is the torque viscosity (Nm.s), and N is the impeller angular speed (rev/s).

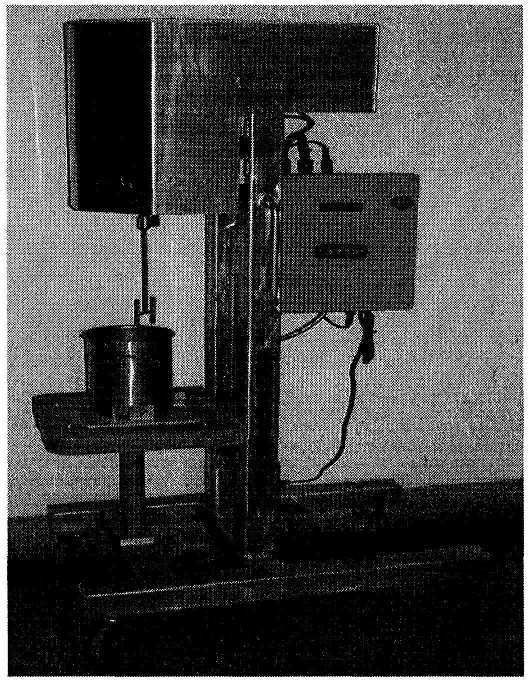

Fig. 3.3 IBB rheometer

The torque is a function of shear rate; the flow resistance (G) is related to the yield stress, and the torque viscosity is related to the dynamic viscosity; although the G and H values are instrument-dependent properties, by means of proper calibration, they can be related to the yield stress τ_y (Pa) or to the dynamic viscosity μ (Pa.s), which are two fundamental rheological material properties.

In testing, the wet-blended castable mix is poured into the sample bowl of the rheometer and shear stress is applied at time intervals during a measuring cycle of controlled time according to viscosity variation speed (or setting speed) of the castable sample. The resulting curves (torque vs. impeller speed) are used to evaluate rheological behavior of the castables. A typical rheological curve (shear rate vs shear stress or torque) is shown in Figure 3.4.

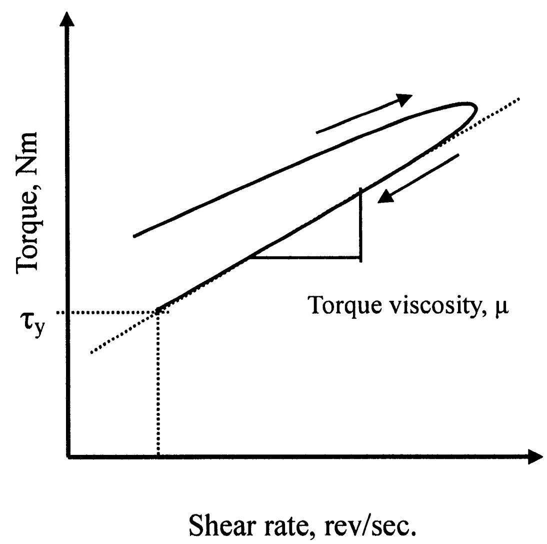

Fig. 3.4 Schematic curve of shear rate vs torque showing rheological property

(4) Methods for studying high temperature mechanical properties

A. Tests for strength properties at elevated temperatures

Three point bending method was used for testing the following properties: (1) Hot modulus of rupture (HMOR) at 1300°C and 1400°C for ten specimens (A series and S series); (2) Modulus of rupture-temperature (MOR–T) relationship at elevated temperatures up to 1400°C for two specimens (A8 and S8); (3) Stress-strain relationship at different temperatures from room temperature (RT) to 1200°C under 500N load for one specimen (S8).

B. Tests for thermal shock resistance (TSR)

(1) Residual strength ratio was determined after one thermal shock cycling from 1200 °C to water-cooling (ΔT=1200 °C) for ten specimens.

(2) Critical temperature difference (ΔT_c) was determined from residual strength–ΔT curves at ΔT from 400 °C to 1300 °C for two specimens (A8 and S8).

The specimen size for the above tests is 160 × 40 × 40mm, except for stress-strain tests which were 125 × 25 × 25mm.

The microstructure of the specimens after HMOR measurements was observed by SEM to analysis the relationship between high temperature mechanical properties and microstructures.

CHAPTER 4. RHEOLOGY OF BAUXITE-BASED SILICON-CARBIDE CONTAINING CASTABLES

4.1 SYNTHESIS

As the first segment of the experimental work, this chapter presents the results of the investigation on rheological properties of matrixes of bauxite-based castables and of bauxite-based castables, containing SiC, with low CA cement content (up to 6%), and the results of high temperature mechanical properties determination (including high temperature strength properties at elevated temperatures, stress-strain relationships and thermal shock resistance) for those bauxite-based SiC-containing castables. The chapter is composed of three papers which have been already published.

For such well known systems as bauxite-based SiC containing castables, no significant differences have been detected, between rheological behaviour of the matrixes and that of the mixes (containing aggregates).

In this chapter, tackling high quality bauxite and low cement containing castables, it will be firstly confirmed, what some other researches had revealed previously [42~44]: both microsilica and ultra fine alumina can be used as fillers to improve the rheological behaviour of such castables, and that microsilica is much more effective than ultra fine alumina. To optimize the thermomechanical properties, it is also reconfirmed that 25/75, in this work, or 30/70 [66] ratio of ultra fine alumina to microsilica is an optimum choice. The truly significant new result is that this part of the study was able to reveal the role of the particle size distribution (PSD) on the rheological properties, showing that it is not only a matter of adjusting the ultra fine content but the complete PSD. This is an important fact when it will be time to optimize the design of the ultra low cement, alumina based castables with additions of graphite, as it will be seen in the next chapter.

4.2 RHEOLOGICAL BEHAVIOR OF THE MATRIXES OF BAUXITE-BASED CASTABLES

This is the title of paper which has been published in "CHINA` S REFRACTORIES", Vol. 12, No. 3, 2003, 7~12.

4.2.1 Abstract

Rheology of castables is greatly affected and controlled by the rheological behavior of their matrix. In this work, the rheological properties of bauxite-based castable matrix have been studied. The effects of super-fine silica and alumina addition, water/cement ratio, dispersants and bauxite particle-size on viscosity, shear rate and shear stress of the slurries have been investigated. Based on these results, the range of optimum composition of the matrix with good rheological behavior has been obtained.

4.2.2 Introduction

The refractories industry is closely associated with industries that use high temperature. In the new century refractories industry should continue to develop better materials to meet with the more stringent requirement of new high temperature technologies. An important achievement of refractories development worldwide in the past two decades is the fast progress of monolithic materials, especially refractory castables.

The progresses in castables predominantly depend upon three important issues: ① fabrication and selection of fillers and binders for low cement, ultra-low cement and zero cement bonding castable system; ② installation techniques of castables (from vibrating to self-flowing, pumping and shotcreting); ③ operating condition limitations (maximum temperature of use, chemical and mechanical constraints such as slag or alkali corrosion, hot metal impact, sudden thermal shock etc.).

The main purpose of this work is to evaluate rheological behavior of matrix of bauxite-based castables by studying the influences of ultra-fine powders (silica and alumina), water/cement ratio, dispersant additions and bauxite particle size on apparent viscosity and shear rate/shear stress relationship of slurry. Goals of the work are to understand rheological characteristics of castable matrix in order to optimize the matrix composition and later on to correlate the performance characteristics to the rheological behavior of the castables.

4.2.3. Experiments

(1) Experimental method

The rheological behavior of slurry is studied by means of rotational coaxial double cylinder viscometer (NXS-11A model). The viscosity and shear stress can be calculated by the following formula:

$$\eta = \tau / D \quad (4\text{—}1)$$

$$\tau = T / 2\pi R_1^2 h \quad (4\text{—}2)$$

$$D = 2\omega R_2^2 / (R_2^2 - R_1^2) \quad (4\text{—}3)$$

$$= [(\pi/15) \cdot R_2^2 / (R_2^2 - R_1^2] \cdot n = K \cdot n$$

Where η= viscosity (Pa·s), τ = shear stress (Pa), D = shear rate (sec.-1), R_1 = radius of the inner cylinder-rotor, h = height of the inner cylinder, R_2 = radius of the outer cylinder-rotor, T = Torque, $\omega = 2\pi n/60$, angular velocity, n = rotor speed.

The viscosity and shear stress of slurries, under different shear rates, are measured at varying rotation speed. The viscosity curve (η vs D) and flow curve (τ vs D) are then used to appreciate their rheological behavior.

(2) Slurry preparation

The raw materials used for the tests include:

Bauxite fines: $Al_2O_3 \geq 85\%$, < 200 mesh (D50 = 38.5μm), < 325 mesh particle size (D50 = 14.1μm).

SiC: ≥ 96 %, < 200meshes,

CA cement (Secar 71, Al_2O_3 69.0 ~ 72.2 %, CaO 27.0 ~ 30.0 %, D50 = 12 μm,),

Microsilica: $SiO_2 \geq 95.0$ %, (<1.5μm, D50 = 0.5μm),

Ultra-fine alumina: $Al_2O_3 \geq 98.5$ %, (< 4.0μm, D50 =1.8μm).

The raw materials are uniformly mixed according to the formulation, and then well blended with water additions to form slurries within 2 minutes, for measurement of various rheological parameters.

(3) Experiments

The rheological behavior of castable matrix with multiple components is influenced by various factors. In this work, effects of ultra-fine powders (silica and alumina), water/cement ratio, dispersant additions and bauxite fines ratio on apparent viscosity and rheological parameters of matrix are investigated. The formulations are shown in Tables 4.2.1~ 4.2.6 as follows. For each formulation, the same amount of SiC 16 % and of water 19 % (except formulation 6), the same amount cement 5 % (except formulation 4) and the same amount dispersant 0.12 % (except formulation 5) are always used. The remaining composition of the fine powders is constituted by bauxite fine -200mesh only (except formulation 6), and so in formulation 1, sample 1 contains 79 % bauxite and sample 2 contains 77 % bauxite, the same rule apply to all other formulations.

Table 4.2.1 Formulations to test the effects of microsilica

Sample No.	1	2	3	4	5
Fine powders, %	95	93	91	89	87
Micro-silica, %	0	2	4	6	8

Table 4.2.2 Formulations to test the effects of ultra-fine alumina

Sample No.	1	2	3	4	5
Fine powders, %	95	93	91	89	87
Ultra fine alumina, %	0	2	4	6	8

Table 4.2.3-a Formulations to test the effects of mixed ultra-fine powders at level of 4% ultra fine alumina

Sample No.	1	2	3	4	5	6	7	8
Fine powders, %	90	89	88	87	86	85	84	83
Micro-silica, %	1	2	3	4	5	6	7	8
Ultra fine alumina 4%								

Table 4.2.3-b Formulations to test the effects of mixed ultra-fine powders at level of 3% microsilica

Sample No.	1	2	3	4	5	6	7	8
Fine powders, %	91	90	89	88	87	86	85	84
Ultra fine alumina, %	1	2	3	4	5	6	7	8
Microsilica 3 %								

Table 4.2.3-c Formulations to test the effects of mixed ultra-fine powders at a total content of 7% of ultra fine alumina and microsilica

Sample No.	1	2	3	4	5	6
Micro-silica, %	0	2	3	4	5	6
Ultra fine alumina, %	6	5	4	3	2	0

Table 4.2.4 Formulations to test the effects of cement contents

Specimen No.	1	2	3	4	5	6	7	8	9	10
Fine powders, %	92	91	90	89	88	87	86	85	84	83
Cement, %	1	2	3	4	5	6	7	8	9	10

Ultra fine alumina 4 % ; microsilica 3 %

Table 4.2.5 Formulations to test the effects of dispersants

Bauxite fine	SiC	Microsilica	Ultra-fine alumina	Cement
72 %	16 %	3 %	4 %	5 %

The dispersants used include Castament FS-20 (organic dispersant), sodium tripolyphosphate, sodium hexameta- phosphate, sodium citrate, sodium polyacrylate, calcium lignosulphonate and sodium lignosulphonate. The tested range of their amounts is from 0.06 wt% to 0.28 wt %.

Table 4.2.6 Formulations to test the effects of bauxite fine particle sizes

Sample No.	1	2	3	4	5	6
-325 : -200 mesh value	1:5	1:2	1:1	2:1	5:1	1:0

Ultra fine alumina 4 %; microsilica 3 %; water 22%

4.2.4. Results and discussions

4.2.4.1 Effect of ultra-fine powders on rheological behavior

Fig. 4.2.1 shows the effects of microsilica and ultra fine alumina on viscosity. The results indicate that with increase of microsilica content in slurry, its viscosity tends to reduce, but with increase of ultra fine alumina content, viscosity shows a slight increase.

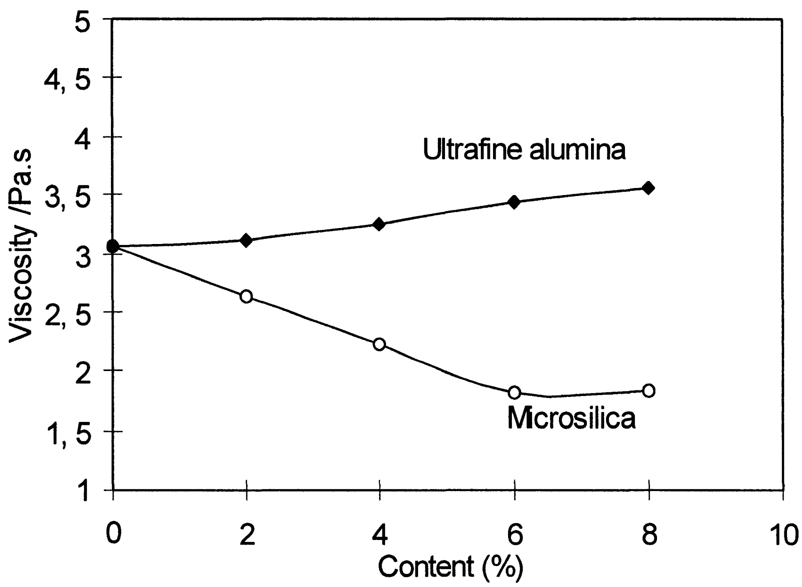

Fig. 4.2.1 Variation of viscosity (η) with ultra-fine powders (silica, alumina) content of slurries

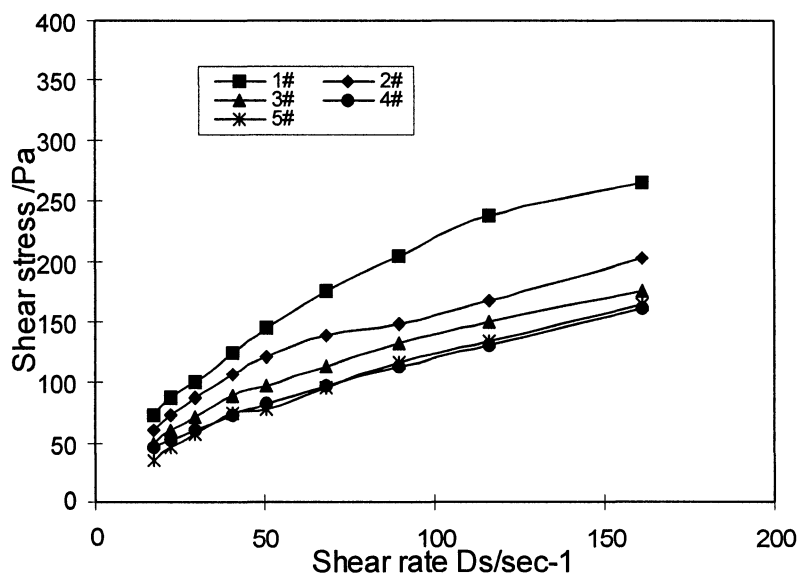

Fig. 4.2.2 Shear rate/shear stress curves for slurries with microsilica

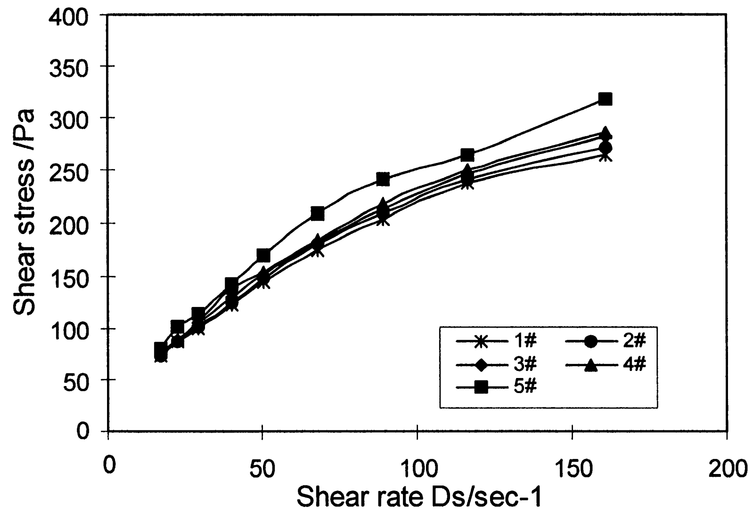

Fig. 4.2.3 Shear rate/shear stress curves for slurries with ultra-fine alumina

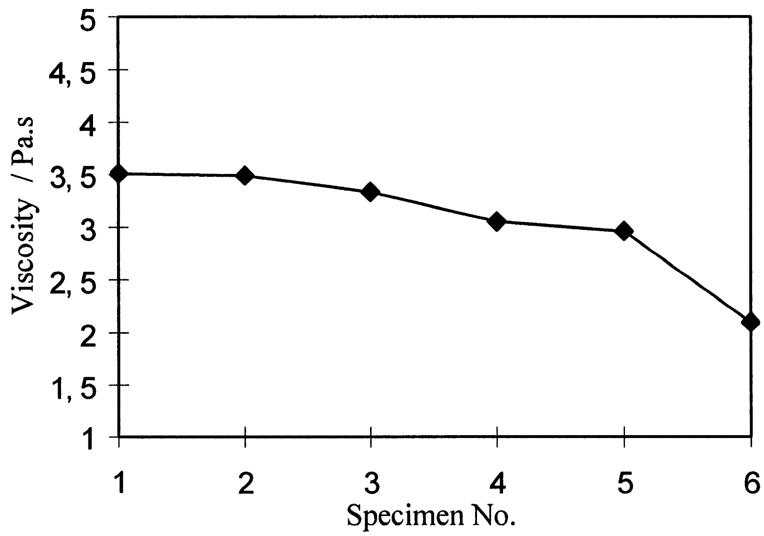

Fig. 4.2.4 Variation of viscosity (η) with uf-Al_2O_3/uf-SiO_2 ratio, as per formulation 3C

Fig. 4.2.2 and 4.2.3 show the effects of microsilica and ultra fine alumina on shear rate and shear stress. The results show that with increase of ultra fine powder amount, the shear stress of slurry with microsilica is decreased and that of slurry with ultra fine alumina is increased. From the above, it maybe concluded that microsilica addition contribute significantly to the improvement of rheological properties, but ultra fine alumina addition exhibits negative effect on rheological behavior. From Fig. 4.2.2 and 4.2.3, it can be also seen that their rheological behavior follows a Bingham flow pattern. The yield stress (τ_y) of slurry with ultra fine alumina is greater than that of slurry with microsilica. For given stress $\tau \leq$ yield τ_y, the slurry remains static and no flow occurs; at stress $\tau >$ yield τ_y, plastic flow occurs.

Fig. 4.2.4 shows the effects of simultaneous additions of microsilica and ultra fine alumina in different ratio on the rheological behavior. It can be seen, once more, that the contribution of microsilica to the improvement of the rheological properties is greater than that of ultra fine alumina.

This later viewpoint is verified by further experiments on the effect of mixed additions, (1) with ultra fine alumina addition fixed at 4%, varying the microsilica addition from 2 % to 8 %; (2) with microsilica addition fixed at 3 %, varying ultra fine alumina from 1% to 8 %. Results on viscosity are shown in Fig. 4.2.5. Fig. 4.2.6 and 4.2.7 (shear rate and shear stress curves) show clearly the Bingham flow pattern.

From the above results, it maybe concluded that the rheological behavior of slurry is mainly depending on the amount of addition as well as the properties and characteristics of the micro powders used. In a system without microsilica, attractions between fine particles would lead to formation of flocculation structure in which free water is trapped. Therefore, their flowability is reduced; viscosity and shear stress are increased. When microsilica is added, the microsilica particles being smaller, disrupt the flocculation structure of the slurry and release the free water, resulting in a better dispersion of particles in the slurry. So flowability is increased, viscosity and shear stress are decreased. Study by Myrhe on the influence of super powders in high alumina castables shows also similar result that microsilica is much more effective in terms of packing [1].

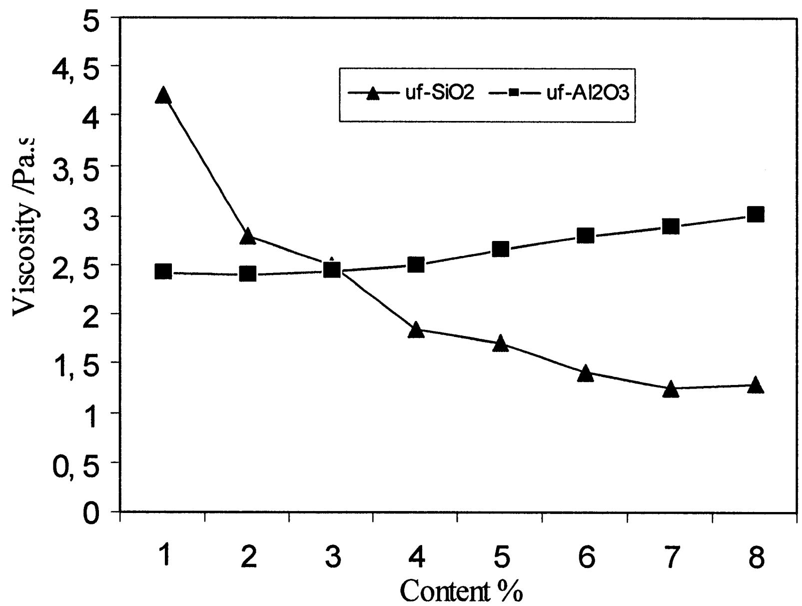

Fig. 4.2.5 Variation of viscosity (η) with microsilica content (uf-Al_2O_3 fixed at 4%) and with ultra fine alumina content (microsilica fixed at 3%).

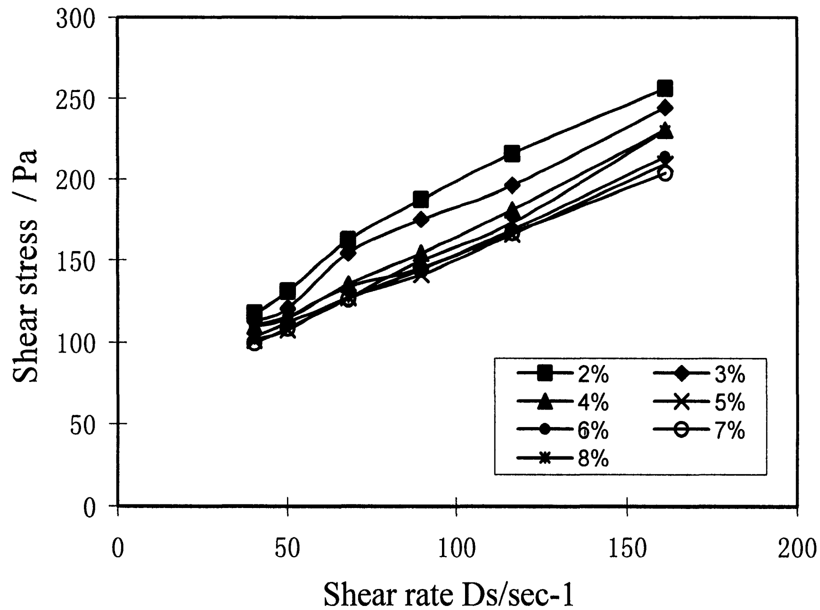

Fig. 4.2.6 Shear rate/shear stress curves for slurries with microsilica (uf-Al_2O_3 fixed at 4%)

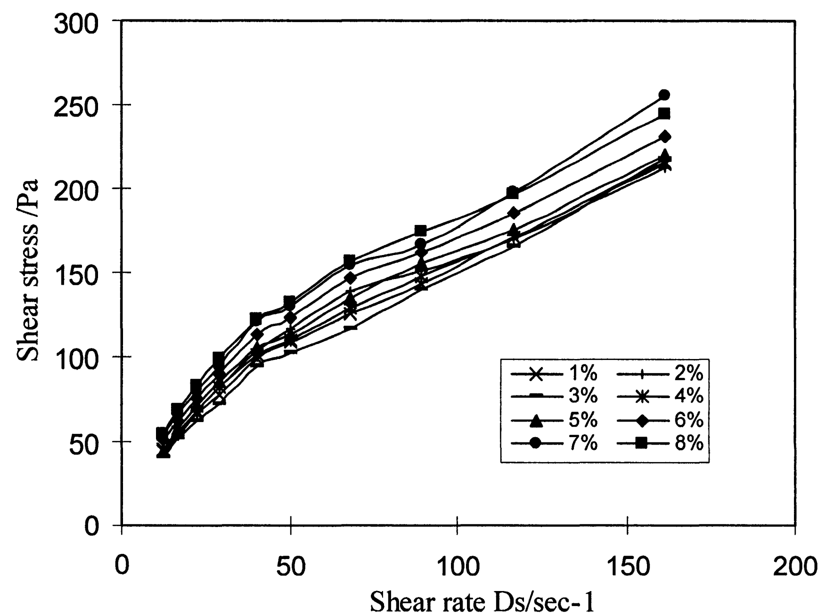

Fig. 4.2.7 Shear rate/shear stress curves for slurries with ultra fine alumina (microsilica fixed at 3%)

4.2.4.2 Effect of water/cement ratio on rheological behavior

For these tests, water content is fixed at 19 % and cement content is varied from 1 % to 10 % which means water/cement ratio varies from 19/1 to 1.9/1. Results are shown in Fig. 4.2.8 and 4.2.9. The apparent viscosity and shear stress are slightly increased with increasing content of cement, up to a water/cement ratio of 19 : 9. This is because at low water/cement ratio, the reaction between water and cement is not completed in the slurry. Fig. 4.2.9 shows that their shear stress and shear rate curves display plastic flow rheological behavior.

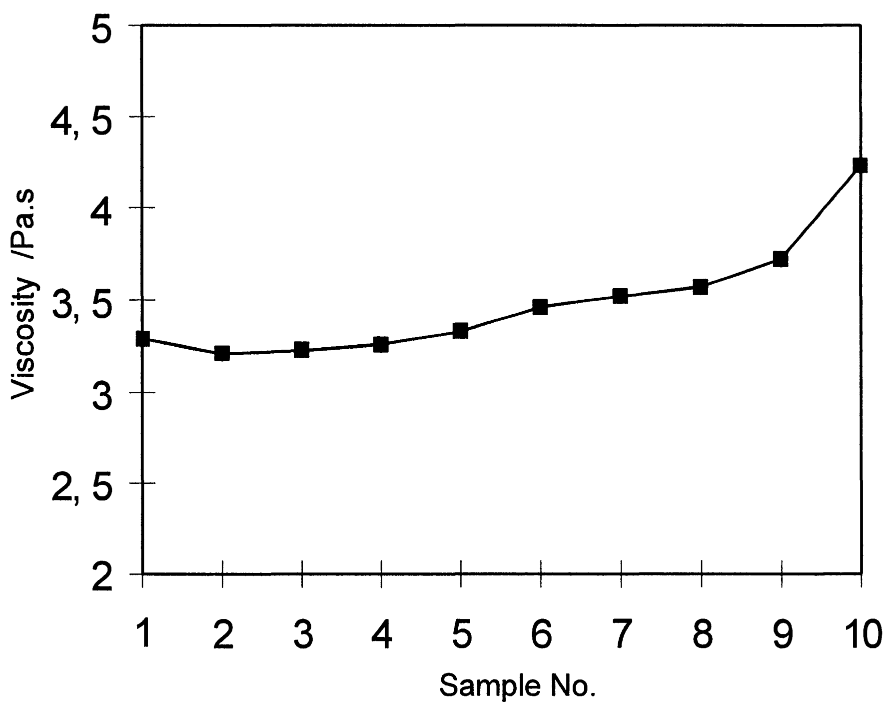

Fig. 4.2.8 Variation of viscosity (η) with water/ cement ratio (W/C = 19:1 to 19:10 from sample 1 to 10)

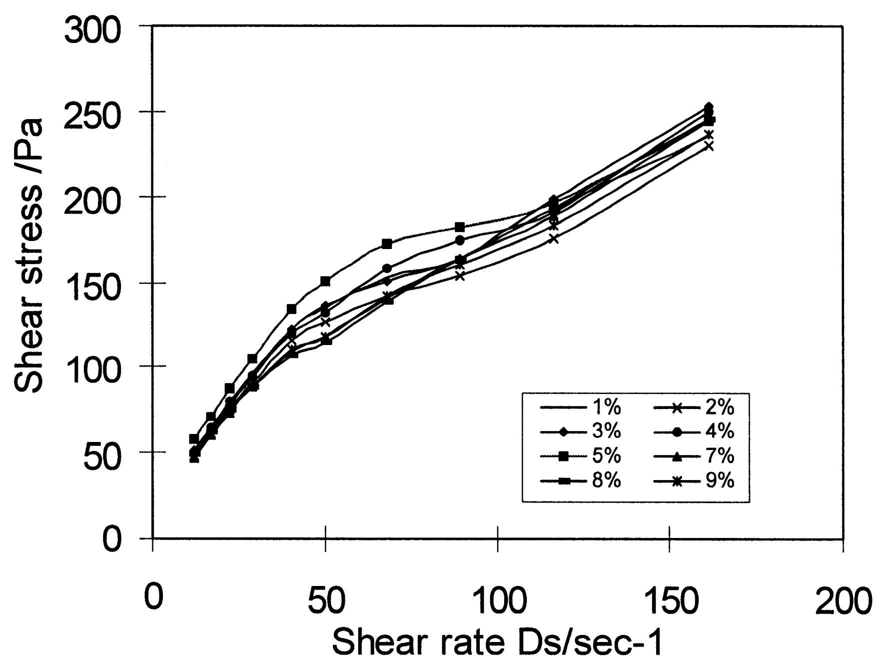

Fig. 4.2.9 Shear rate/shear stress curves for slurries with water/cement ratio (W/C)

4.2.4.3 Effect of dispersants on rheological behavior

The castable matrix behaves in a manner similar to a particulate suspension. Therefore, the dispersion of particles in the matrix is an essential requirement to obtain castables associating high flowability with low water content. Furthermore, dispersion inhibits the formation of agglomerates that can hinder optimum particle packing and affect the castable final mechanical strength.

Matrix dispersion can be accomplished by increasing the surface charges of particles in the slurry. An effective method for this is to use a suitable dispersant. In this part of the work, the effect of seven dispersants on the rheological behavior of a slurry has been investigated and compared in order to elucidate the relevant characteristics. The dispersants used for the tests include: Castament FS-20 (an organic chemical product); sodium tripolyphosphate; sodium hexametaphosphate; sodium citrate; sodium lignosulphonate; sodium polyacrylate and calcium lignosulphonate. Results are shown in Fig. 4.2.10, 4.2.11 and 4.2.12. From Fig. 4.2.10, the dispersants maybe classified into two groups: (1) with good dispersing effect — Castament FS-20, sodium tripolyphosphate, sodium citrate, sodium tripolyphosphate and sodium hexametapho- sphate (η=1.96 ~ 410Pa.s); (2) with poor dispersing effect—sodium hexametapho-sphate, sodium lignosulphonate, sodium polyacrylate, calcium lignosul-phonate (η=18.4 ~ 98.7 Pa.s). Among group (1) dispersant, FS-20 is the most effective in reducing viscosity (η=1.96 Pa.s). From the curves in Fig. 4.2.11 and 4.2.12, it can be seen that the shear stress and yield stress of FS-20 are noticeably lower than those of sodium tripoly-phosphate.

The yield stress is an important parameter which defines whether or not a system is well-dispersed [(2)]. This parameter is defined as the minimum stress necessary to cause flow, which indicates under stress actions, the dispersant weakens the structure of attracted particles and promotes homogenization of the slurry. This means that the dispersants do help more effectively dispersion of ultra-fine powders and reduce internal friction between fine particles. Optimum amount of FS-20 addition in this system is 0.2 wt % (see Fig. 4.2.12).

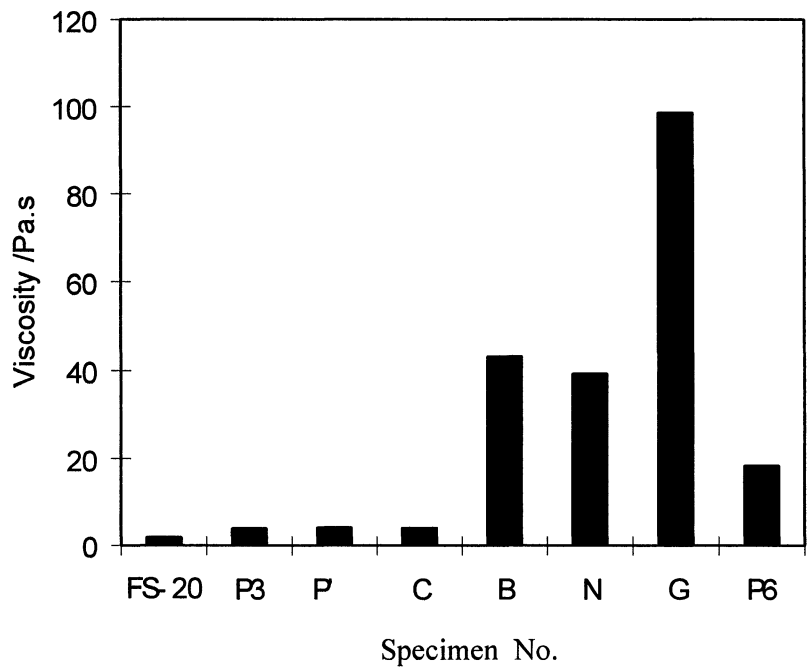

Fig. 4.2.10 Viscosity of slurries with different dispersants addition

FS-20 — Castament

P3 —Sodium Tripolyphosphate

P` — P3 + P6

C —Sodium Citrate

B —Sodium Polyacrylate

P6 —Sodium Hexametaphosphate

N —Sodium Lignosulphonate

G —Clcium Lignosulphonate

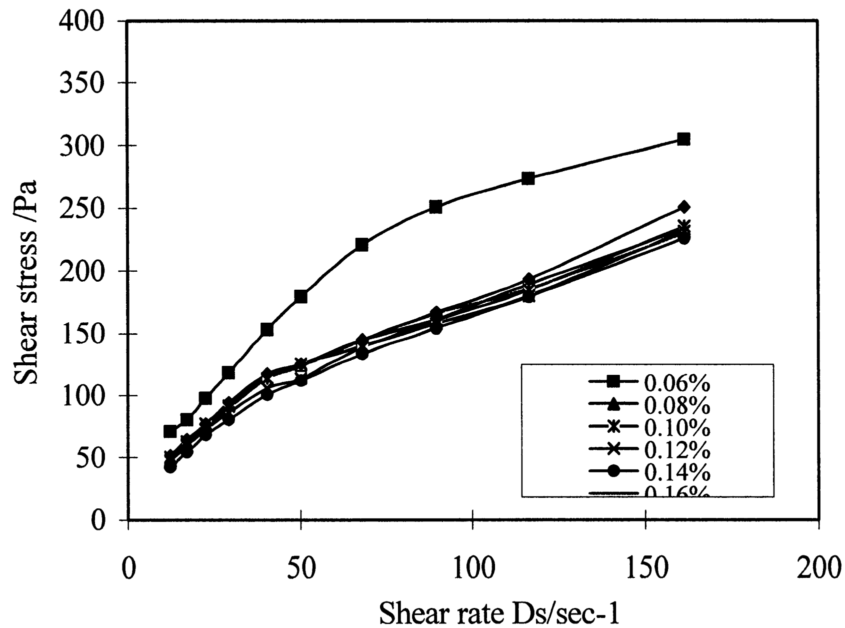

Fig. 4.2.11 Shear rate/shear stress curves for slurries with sodium tripolyphosphate

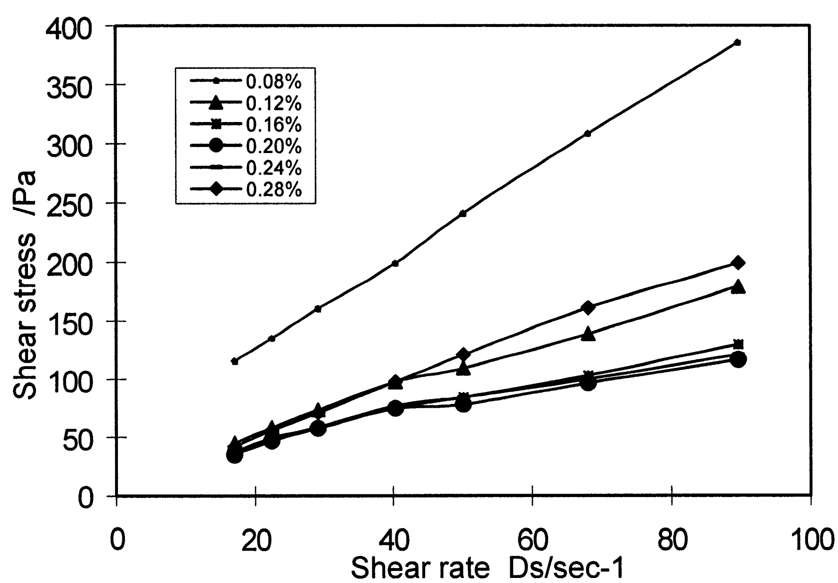

Fig.4.2.12 Shear rate/shear stress curves for slurries with dispersant FS-20

4.2.4.4 Effect of particle size of bauxite fines on rheological behavior

The effects of particle size of the bauxite fine powder in the matrix on rheological properties are shown in Fig. 4.2.13 and 4.2.14. Generally, particle size of fine powder used for manufacture of castables is –200 mesh and –325 mesh. To obtain optimum rheological properties of castable matrix, it is necessary to control the fine powder particle size. Results show that in the slurry, bauxite fine particle size with a ratio of less than 2 : 1 (–325 mesh: –200 mesh) has no obvious impact on viscosity. But when the mixing ratio of the two fine powders is over 2 : 1, the resulting viscosity is increased. Measurements on shear rate and shear stress show similar trends. Too much –325 mesh powder displays higher shear stress and yield stress. So the optimum mixing ratio of bauxite -325 mesh and -200 mesh is less than 2:1. Particle size distribution (PSD) is a very important factor that determines the rheological parameters of a castables [(3)]. For castables, the range of particle size distribution is very wide, from micro-particle to coarse grain, e.g. from < 0.1 μm to 5000μm or more. But the range of PSD for matrix slurries is a relatively narrow, e.g. from < 0.1μm to 90μm. So the effect of PSD in slurry on rheological behavior is not as sensitive as that in castables. For slurries, variation in the range of PSD of bauxite fines would lead to only slight changes in rheological characteristics; however, if –325 mesh particles are excessive, the fines tend to agglomerate, resulting in an increase of viscosity and shear stress. Results obtained by Watanable et al. show that when the amount of finer particle in the matrix is excessive, the flow values of castables are reduced [(4)].

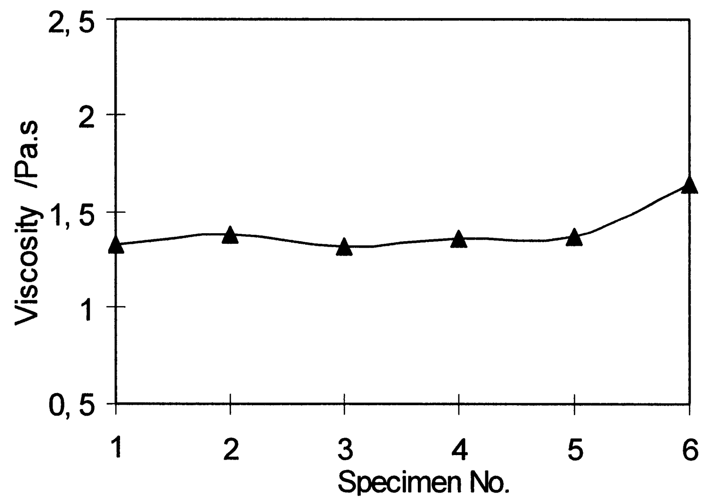

Fig. 4.2.13 Variation of viscosity with bauxite particle size (–325 mesh: –200 mesh)

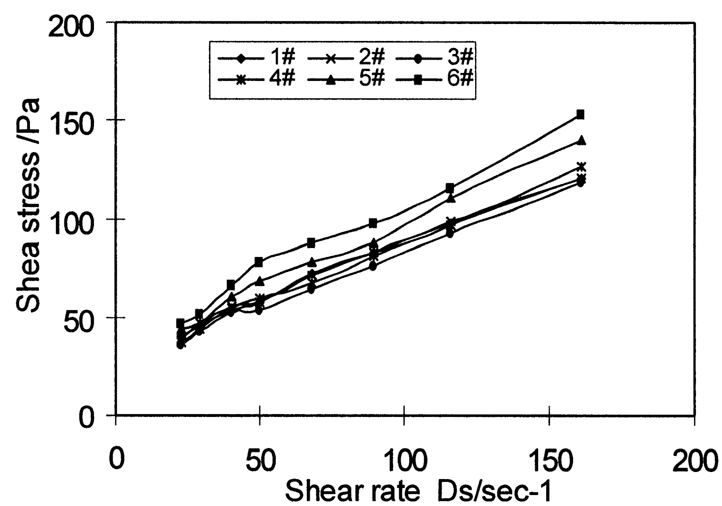

Fig. 4.2.14 Shear rate/shear stress curves for slurries with bauxite particle size (–325 mesh: –200 mesh)

4.2.5 Conclusions

1. The effects of some factors on rheological behavior of a castable matrix have been investigated; ultra fine powder (microsilica and ultra fine alumina) and dispersants are found to be the main controlling factors.

2. Slurry viscosity is noticeably reduced with an increase of microsilica amount, but it is slightly increased with higher ultra fine alumina amount. With either microsilica, ultra fine alumina or combine addition of microsilica and ultra fine alumina, the rheological behavior of slurries exhibits the characteristics of a Bingham fluid.
3. Among the dispersants investigated, FS-20 is the most effective in reducing viscosity, shear stress and yield stress of the slurries. Its optimum addition amount is 0.20 wt %.
4. With a decrease in the water/cement ratio, apparent viscosity and shear stress are slightly increased up to water/cement ratio 19/9

4.2.6 References for chapter 4.2

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3. R. G. Pileggi, V. C. Pandolfelli; Rheology and particle size distribution of pumpable refractory castables, Am. Ceram. Soc. Bull., Vol. 80, (10), 2001, 52—57. (See [32])
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4.3 RHEOLOGICAL BEHAVIOR OF BAUXITE-BASED SILICON CARBIDE CONTAINING CASTABLES

This is the title of a paper which has been published in "CHINA` S REFRACTORIES", Vol. 13, No.1, 2004, 3~10.

4.3.1 Abstract

Low cement (LC) and ultra-low cement (ULC) bauxite-SiC castables are important, high performance monolithic refractories and they have been widely used in iron-making and incinerator linings. In this work, rheological behavior of LC and ULC bauxite-based SiC-containing castables has been studied, including the effects of SiC content and cement content on rheological properties of the castables. The results show that with an increase of SiC and cement content, rheological properties of the castables deteriorate. On the other hand, moderate amounts of SiC (4% ~ 8 %) and of calcium aluminate cement (2% ~ 4%) have a very slight influence on rheological properties, (i.e. when the castables are sheared their torque and yield torque only slightly increase with the shearing speed). The rheological characteristics of the castables are similar to a Bingham fluid and always show a shear thinning behavior.

4.3.2 Introduction

Bauxite-based SiC-containing castables with low cement and ultra-low cement content were initially used in blast furnace troughs, and later also in hot metal vessels to replace bricks. Currently, they are finding use as high performance monolithic refractory materials for the working lining, and they have also been successfully employed in torpedo cars to transport molten iron, blast furnace troughs, molten iron pretreatment ladles, incinerators and as high temperature furnace lining for chemical industries. These SiC-containing castables satisfy the following three property requirements for above mentioned applications: 1) resistance against repeated thermal shock; 2) volume stability at high temperatures; 3) excellent corrosion resistance against molten metals and slags, in particular against desulphurization /dephosphorization fluxes [1,2]. Moreover, the castables are economically effective because of the use of natural bauxite resources.

With the development of new installation techniques of castables, the low cement and ultra-low cement bauxite-based SiC containing castables are now widely installed by wet pumping and spraying. To meet the requirement of modern installation methods, it is necessary to understand the rheological behavior of the castables in order to assess their pumping and spraying ability, as well as placement quality, and also to explore possible avenues for further application areas. In this paper, the rheological behavior of LC and ULC bauxite-based SiC-containing castables has been studied, including the influences of SiC (filler) content and cement content on rheological properties.

4.3.3 Experiments

(1) Raw Materials

The raw materials used for preparation of castables are shown below:

Sintered bauxite: $Al_2O_3 \geq 89\%$, $SiO_2 > 5\%$, as aggregates (5 ~ 0.088mm) and fines (< 200 mesh, D50=38.5μm; < 325 mesh, D50 = 14.1μm).

Silicon carbide fillers: SiC ≥ 96 %, < 200 mesh.

Calcium aluminate cement: (Secar 71, Al_2O_3 69.0~72.2 %, CaO 27.0~ 0.0 %, D50 = 12 μm).

Microsilica: Elkem 971 U, $SiO_2 \geq 97.0$ %, (<1.0μm, D50 = 0.5μm).

Ultra-fine alumina: $Al_2O_3 \geq 98.5$ %, (< 4.0μm, D50 =1.8μm).

(2) Specimen Preparation

An approximate q value of 0.29 from Andreasen's particle size distribution model was used for design of particle size distribution of the castables. The ratio between aggregates (5 ~ 0.088mm size) and fillers was 62/38. Ultra-fine alumina/microsilica (uf-Al_2O_3 / SiO_2) ratio was 25 : 75. Two groups of bauxite-SiC castable specimens were prepared:

1) Fixed 2% cement content, varying SiC addition from 4 wt% to 16 wt%, to study the influence of SiC addition on rheological properties;

2) From above test results, fixed 6 wt% SiC addition, varying cement content from 2 wt% to 4wt%, to study the influence of cement on rheological properties.

The raw materials were uniformly mixed and well blended with 7.1 ~ 7.5% water addition. Castable mix of 10-kg was used for each rheological test.

(3) Experimental method

Immediately after wet blending, the flowability of the castable mix was represented by self-flowing value, measured using a circular cone (Φ70/100× 50mm).

IBB rheometer [3] (shown in Fig. 4.3.1) was used to measure rheological parameters of the castable samples. This rheometer can monitor the applied torque, control the speed of castable shearing and record all the rheological parameters with high accuracy. It consists of a sample bowl and 3/4 HP motor that drives an H-shape impeller with a planetary movement. The imposed torque is gradually increased with different speeds during the test. By recording torque data at different impeller speeds it is possible to calculate yield stress and shear stress values which reflect the rheological behavior of castables. Shearing torque can be expressed in terms of two parameters by the following equation:

$$T = G + HN \qquad (4\text{—}1)$$

Where T is the value of torque applied to the impeller (Nm); G is the flow resistance (Nm); H is the torque viscosity (Nm.s), and N is the impeller angular speed (rev/s).

The torque stress is a function of shear rate; the flow resistance (G) is related to the yield stress, and the torque viscosity is related to the plastic viscosity; Although the G and H values are instrument-dependent properties, by means of proper calibration, they can be related to the yield stress τ_0 (Pa) or to the plastic viscosity μ (Pa.s), which are two fundamental rheological material properties.

For the measurements, the wet-blended castable mix is poured into the sample bowl of the rheometer and shear stress is applied at 5 minute intervals during a measuring cycle of 40 minutes. The resulting curves (torque vs. impeller speed) are used to evaluate rheological behavior of the castables.

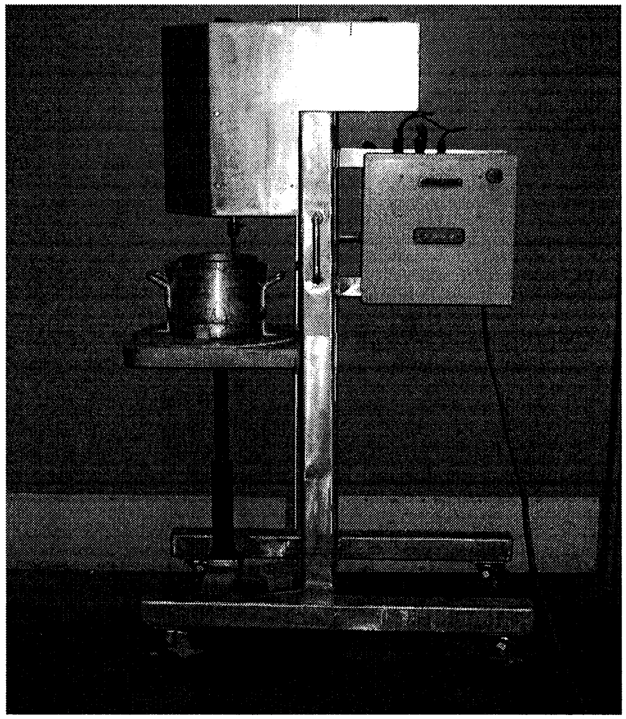

Fig. 4.3.1 IBB rheometer

4.3.4 Results and discussion

4.3.4.1 Effects of SiC addition on rheological behavior

In the rheological tests, for shearing of castables with different SiC content, the water demand slightly increases from 7.1wt% to 7.5 wt% as SiC content is increased. The influence of SiC addition on flowability and rheological behavior are shown in the Fig. 4.3.2 ~ 4.3.7.

From the Fig.4.3.2, it can be seen that the samples without SiC addition and with 4 wt% to 8 wt% of SiC, containing the same water amount, exhibit very similar flowability. But with the increase of SiC content above 8 wt%, the flow value decreases and water demand grows;

the sample with 16 wt% SiC shows the lowest flow value and the highest water amount. It is concluded that the increase in SiC content leads to flowability degradation of the castables and the content of SiC addition in the castables should not exceed 8 wt% in order to insure adequate flowability.

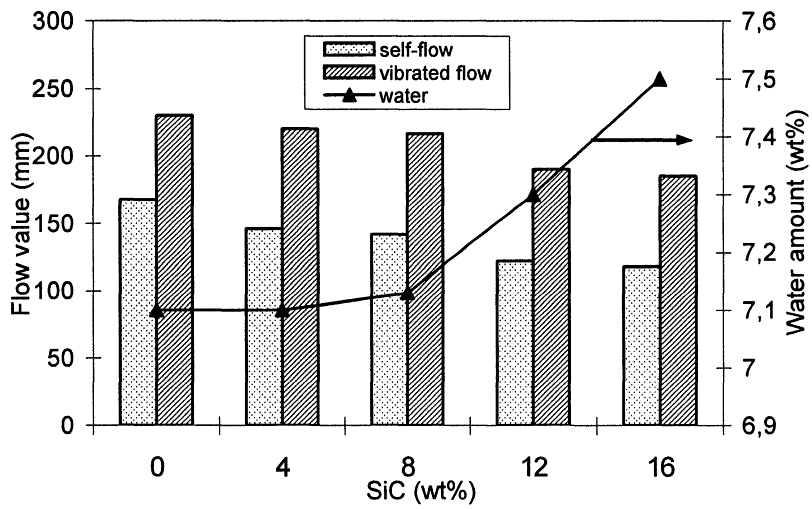

Fig. 4.3.2 Self-flow value and water amount of the samples with different SiC content

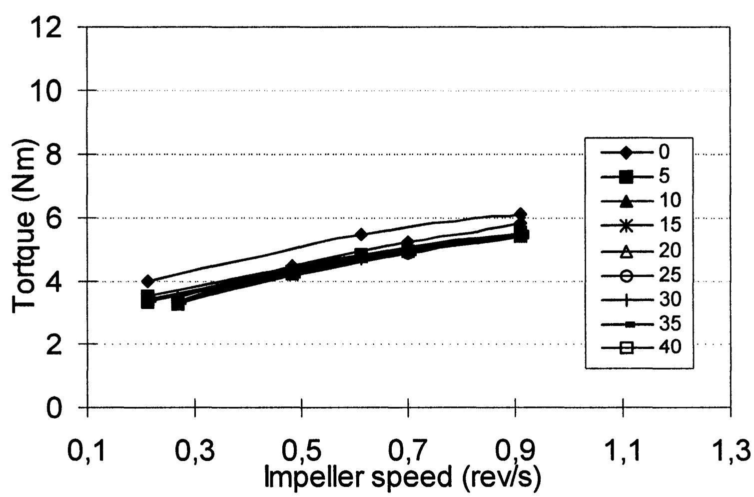

Fig. 4.3.3 Rheological curves of bauxite-based, SiC-free castables

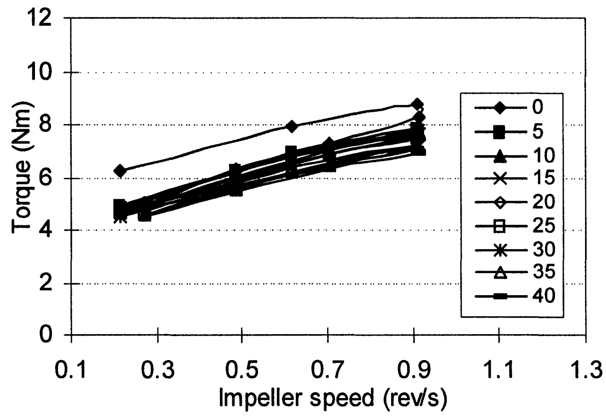

Fig. 4.3.4 Rheological curves of bauxite-based castables with 4 % SiC

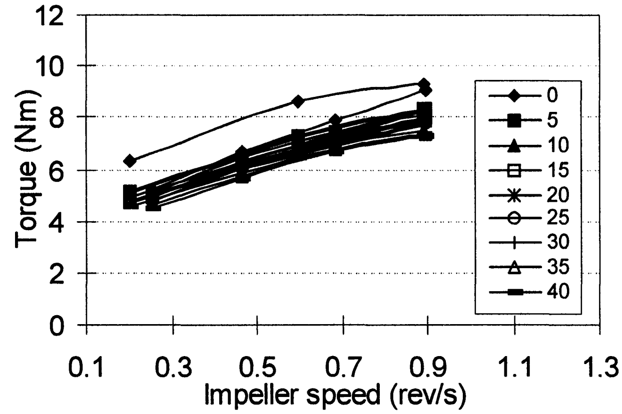

Fig. 4.3.5 Rheological curves of bauxite-based castables with 8 % SiC

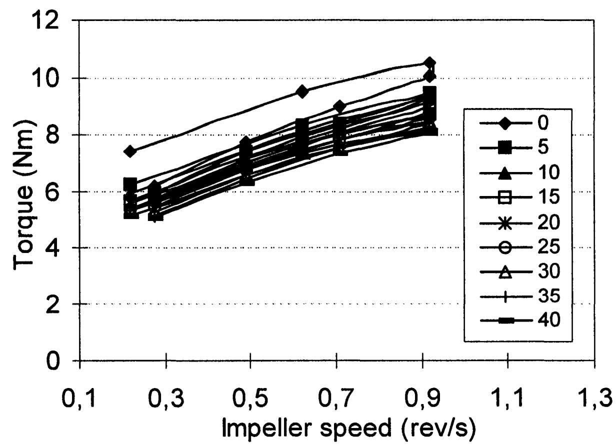

Fig. 4.3.6 Rheological curves of bauxite-based castables with 12 % SiC

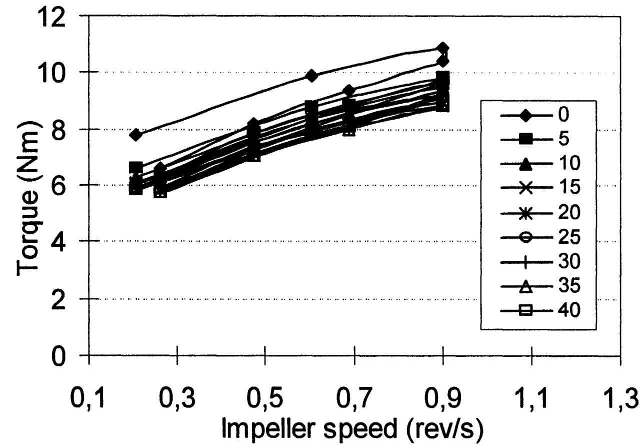

Fig. 4.3.7 Rheological curves of bauxite-based castables with 16 % SiC

It can be seen from the Fig. 4.3.2 ~4.3.7:

(1) The castable sample without SiC addition has better rheological properties than SiC-containing castables, exhibiting lower torque and yield stress values as well as with lower water demand. It also shows a stable rheological behavior during the 40 minute-long tests.

(2) As SiC addition is increased from 4 % to 16 wt%, accompanied with an increase of water content, the rheological behavior is gradually degraded, i.e. shearing torque and yield stress are both increased. The torque and yield stress of specimens with 16 % SiC are the highest, even if water amount is increased up to 7.5 %. From rheological characteristics of the castables, the optimal SiC content should be between 4 % and 8%.

(3) All the castables samples exhibit shear thinning behavior during the 40 minute tests, so they maintain a satisfactory shearing performance long enough for installation. Their flow curves follow a Bingham flow pattern.

Fig. 4.3.8 and 4.3.9 show the variation of torque viscosity (H values) and flow resistance

(G values) of the castables tested. In accordance with the previously mentioned results, they show stable torque viscosity and flow resistance values during the 40 minute tests. The sample without SiC addition shows a noticeably lower torque viscosity and flow resistance values.

As rheological characterization (torque, yield stress, torque viscosity and flow resistance), flowability and adequate working time of the castables is analyzed to evaluate the overall workability of bauxite-based SiC containing castables, it is concluded that optimum content of SiC addition is between 4 % and 8%.

There is no doubt that the two main constituents of bauxite-based SiC containing castables, Al_2O_3 and SiC have excellent refractory properties. The reasons for the negative effects of SiC addition with higher content on rheological behavior may be explained as follows: comparing with the ball mill bauxite powder, silicon carbide has higher specific gravity and higher hardness, as well as mostly irregular particle shapes with many sharp edges. So when silicon carbide particles are used as filler in the castables, they would lead to higher flow resistance and an increase of torque viscosity. When ball mill bauxite fines are partially replaced by SiC filler, higher energy would be needed for shearing. Therefore, the castables with higher SiC content have inadequate rheological properties.

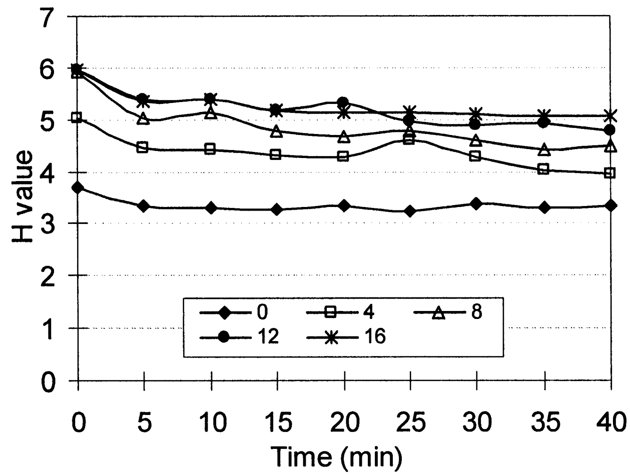

Fig. 4.3.8 The relationship between torque viscosity (H) and testing time.

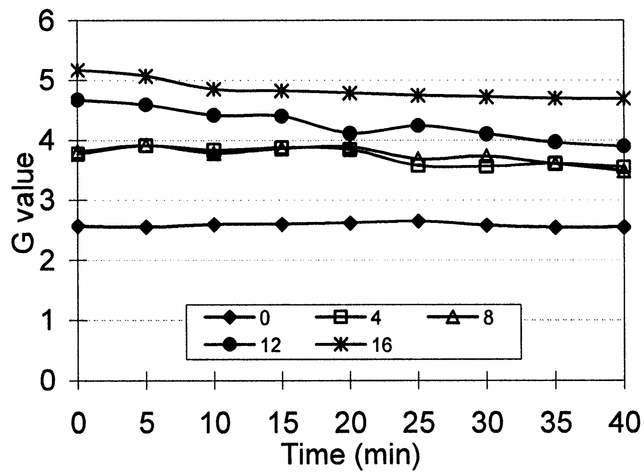

Fig. 4.3.9 The relationship between flow resistance (G) and testing time.

4.3.4.2 Effect of calcium aluminate cement on rheological behavior

For bauxite-based SiC containing castables, the bonding system is mostly composed of microsilica and low amount of calcium aluminate cement; the mode of bonding for the former is agglomeration, whereas that of the latter is hydration. Both take place simultaneously in the castable. In these tests, the effects of calcium aluminate cement content on flowability and rheological properties of the castables have been investigated and their results are shown in Fig. 4.3.10 ~ 4.3.15.

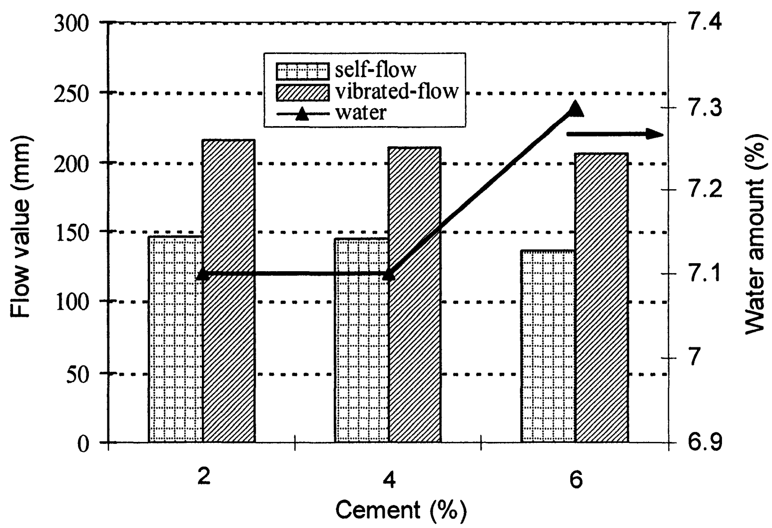

Fig. 4.3.10. Flow value vs water amount of the samples with varying cement content.

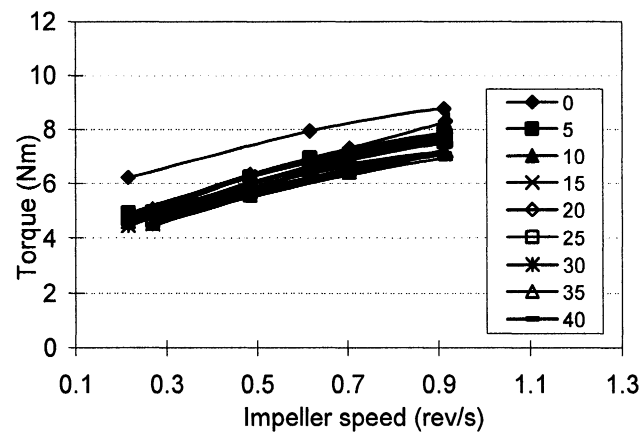

Fig 4.3.11 Rheological curves of castables with 2% cement

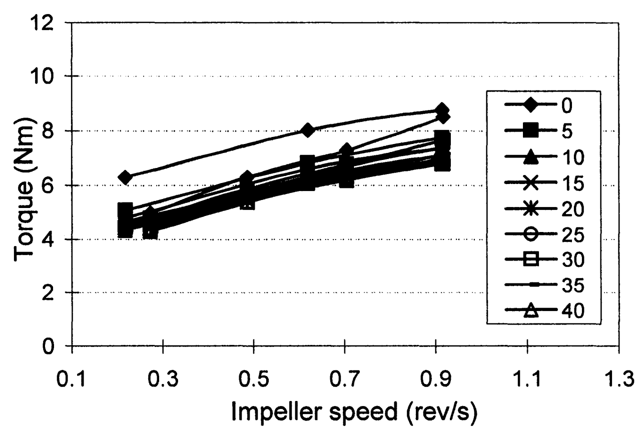

Fig. 4.3.12 Rheological curves of castables with 4% cement

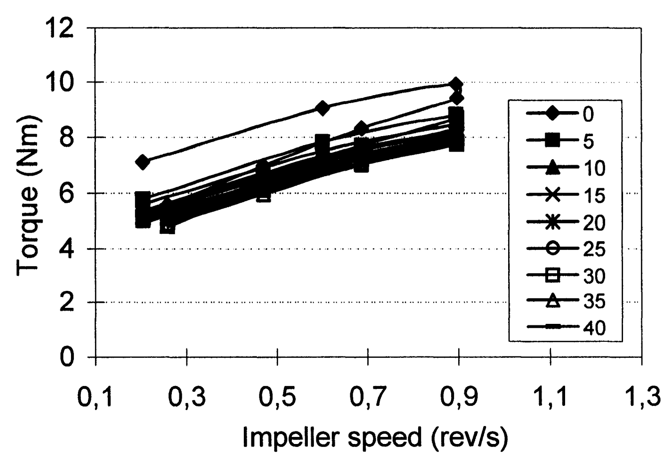

Fig. 4.3.13 Rheological curves of castables with 6% cement

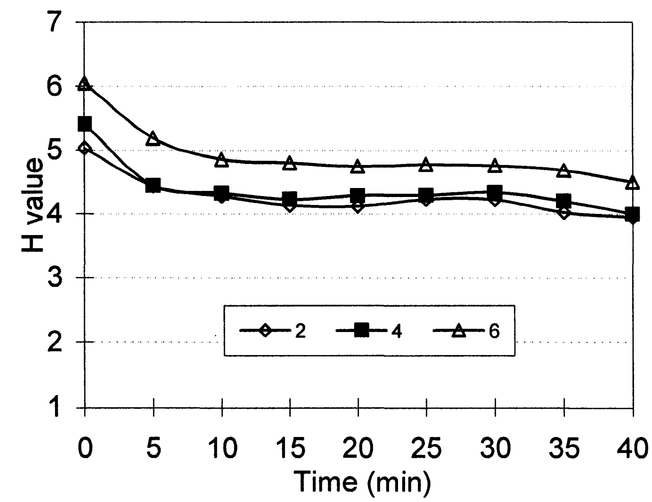

Fig. 4.3.14 The relationship between torque viscosity (H) and testing time

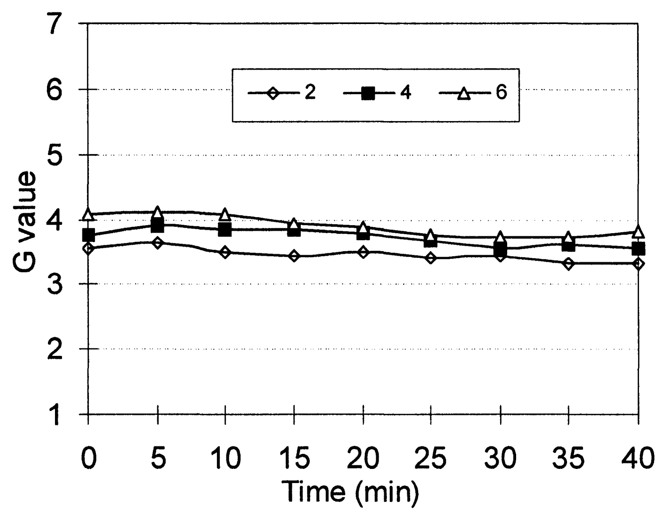

Fig. 4.3.15 The relationship between flow resistance (G) and testing time

It can be seen that the rheological behavior of castables containing different amounts of cement still maintain shear-thinning characteristics, showing Bingham fluid characteristics. There is little variation in torque viscosity (H values) and flow resistance (G values) with testing time, indicating satisfactory installation properties. However, the variation of cement in the samples leads to adverse effects on rheological behavior.

When cement content is 2% to 4% (ultra-low cement), There is very little difference in rheological behavior (torque, yield stress and torque viscosity and flow resistance with testing time) of the castables. But when cement addition reaches 6% (low cement), degradation in the rheological behavior is observed: the torque, yield stress, torque viscosity (H) and flow resistance (G) are increased. Even when water amount is increased from 7.1% to 7.3%, there is still a decrease in flowability of the castable.

Normally, water demand for hydration of calcium aluminate cement in castables is closely related to the amount of cement added. In cement–microsilica bonding system (LC or ULC bonded), cement and microsilica simultaneously contribute to an increase in viscosity until setting. Microsilica contributes to bonding by agglomeration, whereas cement provides bonding through hydration. The hydration mechanism of cement in this system may occur as follows [4]:

$$CA + H \rightarrow CAH_{10} + AH_3 + CH \qquad (4—2)$$

$$\downarrow \qquad \searrow$$

$$C_2AH_8 + AH_3 + CH \rightarrow CH + \text{uf-}SiO_2 \qquad (4—3)$$

$$\downarrow \qquad \nearrow \qquad \downarrow$$

$$C_3AH_6 + AH_3 + CH \qquad (4—4)$$

$$\downarrow\ \text{C–S–H hydrates}$$

Due to hydration of cement, very small particles of amorphous Ca $(OH)_2$ are formed which would react with highly reactive microsilica particles on their surfaces to form calcium silicates hydrates (C-S-H). As a result, hydrated C_3AH_6 and AH_3 phases decrease in quantity. Therefore, in the ultra low cement bonded system, there is no need to increase substantially the water amount for the above reaction. It follows that the effect of cement on rheological behavior is rather weak. However, if cement content in castable is over the range of ultra-low cement castables, the excess cement leads to an increase in viscosity (5) and degradation in rheological properties of the castables, and hence more water has to be added for hydration reaction of the cement. This may probably explain why the effect of cement on rheological behavior in ultra low cement castables is less than that in the low cement castables.

4.3.5 Conclusions

1. Rheological behavior of the bauxite-based SiC containing castables with calcium aluminate cement and microsilica as bonding agent exhibit shear-thinning characteristics and follow a Bingham flow pattern.
2. With variation of silicon carbide content from 0 to 16 wt%, the rheological properties (torque, yield stress, variation of torque viscosity with testing time and flow resistance) of the castables are degraded; optimum SiC content in the castables is 4 % to 8%.
3. In the bauxite-SiC castables with ultra low-cement content, the effect of cement on rheological behavior is very weak. But in the low-cement bauxite-SiC castables, the cement content has a significant negative influence on the rheological behavior.

4.3.6 References for chapter 4.3

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5. F. B. Ye, M. Rigaud, X. H. Liu, X. C. Zhong, "Rheological behavior of the matrixes of bauxite-based castables", China's Refractories, Vol. 12, No. 3, 2003, 7~13. (See [37]).

4.4 HIGH TEMPERATURE MECHANICAL PROPERTIES OF BAUXITE- BASED SIC-CONTAINING CASTABLES

This is the title of a paper which has been submitted and accepted by "CERAMICS INTERNATIONAL", UK, in 2003.

4.4.1 Abstract

High temperature strength properties and thermal shock resistance of ultra low cement bauxite-based SiC-containing castables with two different ultra fine alumina and microsilica ratios (Al_2O_3/SiO_2 = 25/75 and 75/25) have been studied. The results show that SiC addition from 4 wt% to 16 wt% is beneficial for improvement of mechanical and thermal shock resistant properties that may be correlated with microstructrural characteristics.

4.4.2 Introduction

Low cement and ultra-low cement bauxite castables are one of the important, high performance refractory materials, not only due to their high strength, good thermal shock resistance and satisfactory corrosion resistance to slag attack, but also due to their economical effectiveness through use of natural bauxite resources. They have been successfully employed in molten iron torpedo cars, blast furnace troughs and incinerator linings and may have wider applications in high temperature industries. Their mechanical properties at high temperatures are important factors closely related to their application results. Studies on thermo-mechanical properties may provide useful engineering data for estimating the performance of refractory structures under complex stresses and high temperatures, and may also indicate possible trends and avenues for further development in increasing service duration and expanding application areas.

In this paper, high temperature strength properties (hot MOR, MOR-T curves and stress-strain relationship) and thermal shock resistance (residual strength ratio and critical temperature difference) of ultra low cement bauxite-based SiC-containing castables (hereafter referred to as bauxite-SiC castables) have been investigated and the results are discussed in correlation with microstructural characteristics.

4.4.3 Experimental Procedure

4.4.3.1 Raw materials for experiments

The raw materials used for specimen preparation include:

Sintered bauxite: $Al_2O_3 \geq 89\%$, $SiO_2 > 5\%$, as aggregates (5 ~ 0.088mm) and fines (< 200 mesh, D50=38.5μm; < 325 mesh, D50 = 14.1μm).

Silicon carbide as fillers: SiC ≥ 96 %, < 200 mesh.

Calcium aluminate cement (Secar 71, Al_2O_3 69.0~ 72.2 %, CaO 27.0 ~ 30.0 %, D50 = 12 μm).

Microsilica: $SiO_2 \geq 95.0$ %, (<1.5μm, D50 = 0.5μm).

Ultra-fine alumina: $Al_2O_3 \geq 98.5$ %, (<4.0μm, D50 =1.8μm).

4.4.3.2 Formulations of mix specimens

According to Andreasen's particle size distribution model, an approximate q value of 0.29 is used for design of particle size composition of the castable specimens. Two series of bauxite-SiC castable specimens have been prepared. Ultra-fine alumina/microsilica (uf-Al_2O_3

/ SiO_2) ratio is 75:25 for A series and 25:75 for S series; SiC addition varies from 4 wt% to 16 wt%. Their formulations are given in Table 4.4.1.

Table 4.4.1 Formulations of bauxite-SiC castable specimens

Specimen code	*Aggregate Sintered bauxite grogs (%)	Fines (<0.074mm), (%)		Bonding system		
		Bauxite	SiC	CA	Micro-silica	Micro-Al_2O_3
A series *(Al_2O_3 / SiO_2 = 75 / 25 in micro-powder)*						
A0	65	27	0	2	1.5	4.5
A4	65	23	4	2	1.5	4.5
A8	65	19	8	2	1.5	4.5
A12	65	15	12	2	1.5	4.5
A16	65	11	16	2	1.5	4.5
S series *(Al_2O_3 / SiO_2 = 25 / 75 in micro-powder)*						
S0	65	27	0	2	4.5	1.5
S4	65	23	4	2	4.5	1.5
S8	65	19	8	2	4.5	1.5
S12	65	15	12	2	4.5	1.5
S16	65	11	16	2	4.5	1.5

*Aggregate: 5~0.074mm

4.4.3.3 Specimen preparation

The raw materials are uniformly mixed according to formulations, well blended with 5.4% water addition and casted to form specimens of two sizes (160 × 40 × 40mm and 125 × 25 × 25mm). After curing and drying, the specimens are heat treated at 1400 °C for 3 hours under reducing atmosphere. Their porosity is in the range of 13 ~ 18% and MOR is in the range of 5 ~17Mpa, indicating the specimens are fairly well sintered.

4.4.3.4 Test methods

I) Tests for strength properties at elevated temperatures

Three point bending method is used for testing the following properties: (1) Hot modulus of rupture (HMOR) at 1300°C and 1400°C for ten specimens (A series and S series); (2) Modulus of rupture-temperature (MOR–T) relationship at elevated temperatures up to 1400°C for two specimens (A8 and S8); (3) Stress-strain relationship at different temperatures from room temperature (RT) to 1200°C under 500N load for one specimen (S8).

II) Tests for thermal shock resistance (TSR)

(1) Residual strength ratio is determined after one thermal shock cycling from 1200 °C to water cooling (ΔT=1200 °C) for ten specimens (A series and S series).

(2) Critical temperature difference (ΔTc) is determined from residual strength–ΔT curves at ΔT from 400 °C to 1300 °C for two specimens (A8 and S8).

The specimen size for the above tests is 160 × 40 × 40mm, except that for stress-strain tests where 125 × 25 × 25mm was used.

4.4.4 Results and Discussion

4.4.4.1 High temperature strength properties of bauxite-SiC castables

I) HMOR

HMOR of specimens at 1300 °C and 1400 °C under reducing atmosphere of fired bauxite-SiC castable specimens are shown in Fig. 4.4.1.

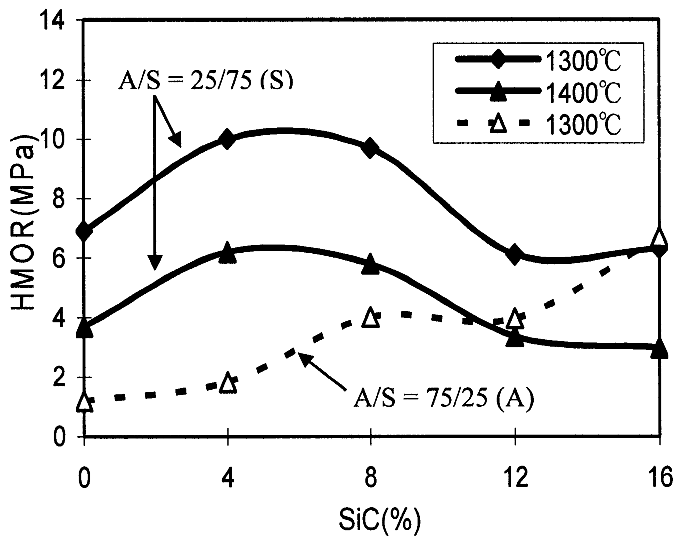

Fig. 4.4.1 Variation of HMOR at 1300°C and =1400°C with SiC contents of bauxite-SiC castable specimens

From Fig. 4.4.1, it can be seen:

(1) HMOR values of S series specimens (ultra fine Al_2O_3 / SiO_2=25/75) at 1300 °C are appreciably higher than those of A series specimens (ultra fine Al_2O_3 / SiO_2= 75 / 25) at all levels of SiC addition (except for 16 wt% SiC).

(2) For A series specimens, HMOR at 1300 °C tends to increase with increase of SiC

addition from 4 to 16 wt%. With 16% SiC addition, HMOR reaches 6.6 MPa which is 5.5 times of that of specimen without SiC (1.2MPa).

(3) For S series specimens, there is noticeable increase in HMOR at 1300 °C and 1400 °C when 4% and 8% SiC is added. With further addition, HMOR tends to decrease. With 12% and 16% SiC addition, HMOR values are close to that of the specimen without SiC. The increase of testing temperature from 1300 °C to 1400 °C leads to considerable decrease of HMOR.

The above results may be interpreted in terms of microstructure: (1) the mineral phases of bauxite castable specimens are essentially corundum, mullite and glass. The microstructure is mainly composed of granular corundum skeleton structure interlaced with mullite crystals. The amount of microsilica added in specimen S0 is 3% more than that in specimen A0 which means the mullite content of the former is 10.65% higher. This significant increase in mullite content contributes to the better HMOR of S series specimens. (2) For A series specimens, when SiC is added, the prismatic SiC crystals are interlaced into the skeleton structure of granular corundum with small amounts of mullite crystals which would lead to a reinforcing effect. This explains the appreciable increase of HMOR with increase of SiC addition in A-series. (3) For S series specimens, the granular corundum skeleton structure is partially filled with more mullite crystals; when 4~ 8% SiC is added, the SiC crystals would be interlaced in the skeleton structure (see Fig. 4.4.2), creating a reinforcing effect. But when 12~6% SiC is added, there is excessive SiC crystals which may disrupt the skeleton structure to some extent, resulting in a weakening effect. This is why there is little or no increase in strength when 12~16% SiC is added in S series specimens.

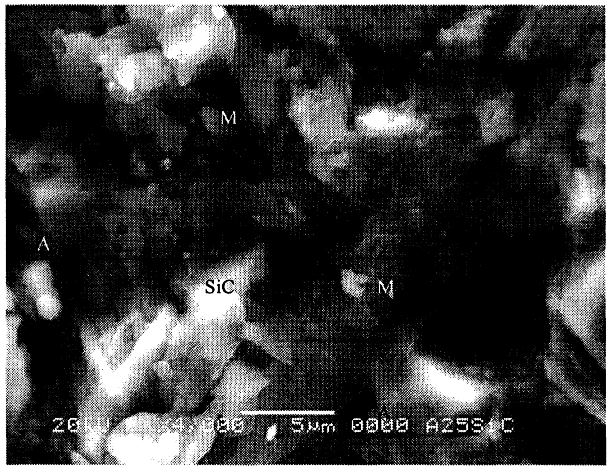

Fig. 4.4.2 SEM photograph of bauxite-SiC specimen (S8)

II) MOR-T curves

Two specimens with 8% SiC addition (A8 and S8) are selected for investigating the changes in MOR with temperature rise from room temperature to 1400 °C. The MOR-T curves obtained are illustrated in Fig. 4.4.3.

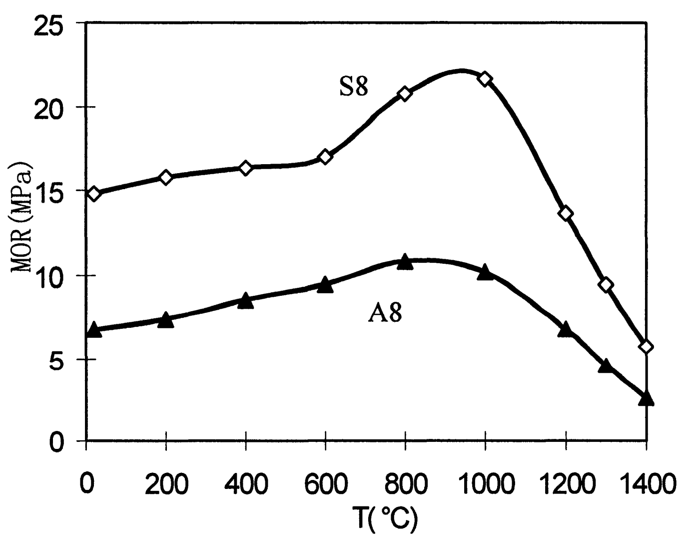

Fig. 4.4.3 MOR –T curves for specimens A8 and S8

The results show that in the low temperature range (20 ~ 600 °C), there is only slight increase of MOR with an increase in temperature. In the medium temperature range (800 ~ 1000 °C), MOR of specimens increases noticeably, reaching a maximum at 800 °C (specimen A8) and 1000 °C (specimen S8), after which strength decreases remarkably.

Zhong has postulated [1] that MOR-T curves of refractory materials may be classified into two types. In type I materials, strength increases with temperature rise up to an inflexion point (Tm), after which strength decreases with temperature rise. In type II materials, there is no strength increase at low and medium temperatures, but at a certain point, strength begins to decrease with temperature rise. In general, materials with two or more crystalline phases belong to type I, whereas materials with one single crystalline phase belong to type II.

It is clear that the above MOR-T curves belong to type I. The increase of strength with temperature rise at low and medium temperatures may be attributed to differential thermal expansion of the main crystals (coefficient of thermal expansion for corundum, mullite and SiC is 8.0-8.5, 5.0 and 4.7×10^{-6} $^{o}C^{-1}$ respectively). The rapid decrease of strength from 1200-1400°C is mainly due to the softening of glassy matrix which would accelerate slip of crystals.

4.4.4.2 Stress-strain relationship

Specimen S8 (size 125×25×25mm) is selected for investigating stress-strain behavior from RT to 1200 °C. In the tests, the maximum stress applied for the experiments is 500N. Changes in strain deformation when stress is applied and released are recorded automatically. The stress-strain curves thus obtained are shown in Fig. 4.4.4 and 4.4.5.

From Fig. 4.4.4 and 4.4.5, the stress-strain behavior may be divided into three stages: (1) Elastic range (RT to 600 °C): the stress-strain relationship is a reversible straight line; only very slight decrease in strain deformation is observed. (2) "plastic flow range" (800 to 1000 °C): the stress-strain curves exhibit a permanent deformation; (3) "viscous flow" range (1000 °C and above): there is prominent strain increase with increase of stress, indicating viscous flow due to softening of the glassy matrix[2,3].

According to Zhong et al. [4], thermo-mechanical behavior of sintered bauxite refractories is determined largely by microstructural characteristics dependent on two principal factors: (1) The amount and viscosity of the glassy matrix (glass effect); (2) The extent and mode of crystal-to-crystal contact or bonding (crystal effect).

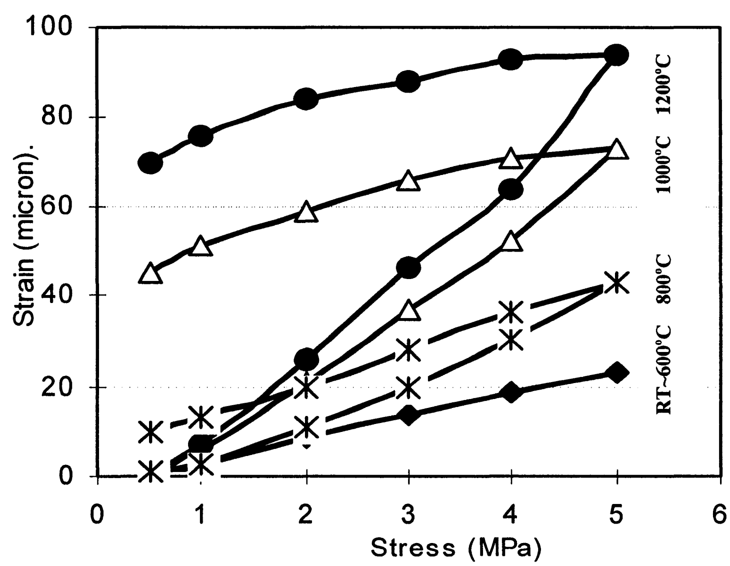

Fig. 4.4.4 Stress-strain curves of specimen S8 (RT~1200 °C) under max. 500N load

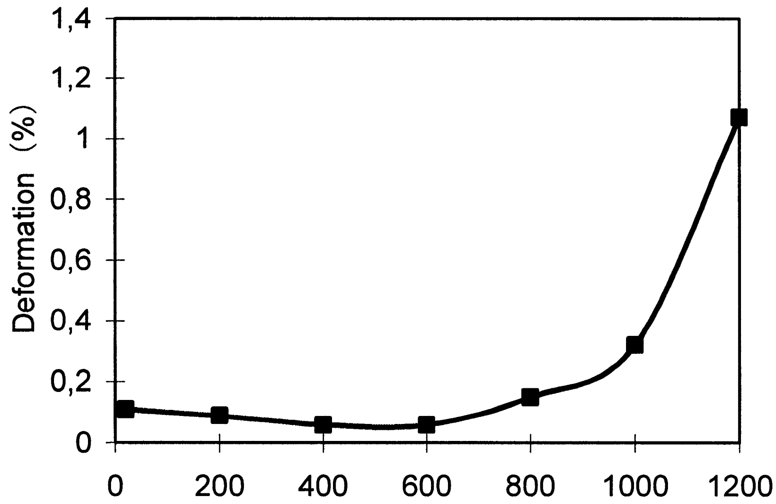

Fig. 4.4.5 Variation of strain deformation of specimen S8 with temperature under 500N load

In this work, in the low temperature range prior to incipient plasticity (up to 600 °C), resistance to stress depends mainly on the resistance of the individual corundum, mullite and SiC crystals and also on their degree and mode of bonding. At this stage, glass effect could only play an insignificant role, if any at all. In the plastic flow range, both crystal effect and glass effect would simultaneously exert influence, but the controlling factor would be the crystal effect. In the viscous flow range (1000 °C and above), the glass effect is the dominant factor; the glassy matrix tends to soften resulting in rapidly increased strain deformation under stress.

4.4.4.3. Thermal shock resistance (TSR)

A) Residual Strength Ratio at ΔT=1200 °C

In TSR tests, the specimens were heated to a predetermined temperature (T) and then quickly quenched in running water. After drying, the residual rupture strength (σ_R) was measured and compared with the original strength (σ_f). Residual strength ratio (σ_R/σ_f) at temperature difference ΔT is a criterion for evaluating TSR.

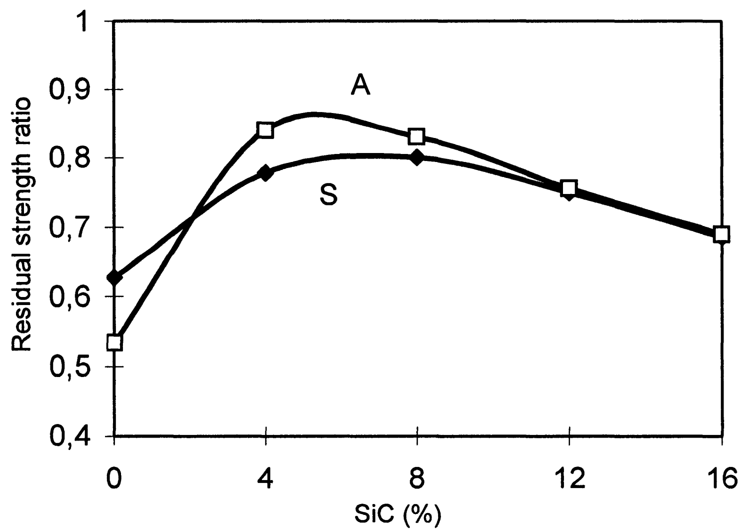

Fig. 4.4.6 Variation of residual strength ratio (σ_R/σ_f) with SiC addition (ΔT=1200°C) for bauxite-SiC castable specimens (A and S series)

Residual rupture strength ratio at ΔT=1200 °C of the two series of sintered bauxite-SiC castable specimens (series A and S) are determined by measuring MOR before and after the thermal shock cycling. The results shown in Fig 4.4.6 clearly demonstrate that compared with specimens without SiC, the residual strength ratio of SiC-containing specimens is increased; with increase of SiC addition, it also tends to increase. The maximum residual strength is attained at 4 ~ 8% SiC addition.

B) Critical temperature difference (ΔTc)

Two specimens with 8% SiC (code A8 and S8) are selected for determining the changes in MOR after thermal shock at ΔT from 400 °C to 1300 °C. From the results (shown in Fig.

4.4.7), it can be seen: for both specimens, there is no change in strength up to 800 °C, after which strength tends to decrease appreciably. This means that the critical temperature difference (ΔTc) of both specimens is 800 °C. According to Hasselman theory [5], ΔTc indicates the ability of material to resist damage from temperature changes. The higher the ΔTc, the better the TSR. In our case, when ΔT is 400 ~ 800 °C, the inside structure of specimens is not affected by thermal shock. But when ΔT is 800 °C ~1300 °C, the inside structure of specimen is partially disrupted by the thermal shock, causing thermal stresses to develop that extend original cracks and initiate formation of new cracks.

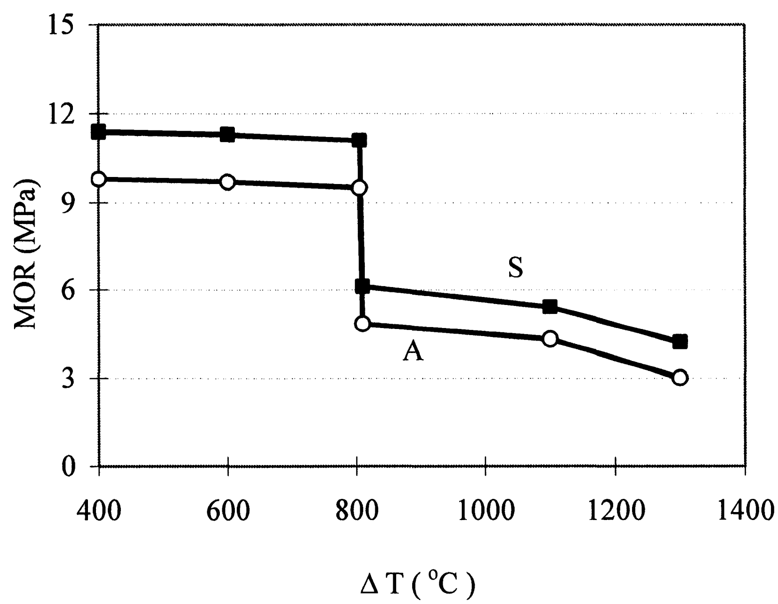

Fig. 4.4.7 Variation of residual strength with ΔT for specimens A8 and S8

The improvement of TSR of bauxite-SiC specimens by SiC addition may be due to: (1) higher thermal conductivity, lower thermal expansion and higher strength of SiC. (2) Its mostly prismatic or elongated crystals are more resistant to thermal stresses. When they are interlaced into the corundum-mullite structure in bauxite-based castable specimens after sintering, not only hot strength is increased due to reinforcing effect but also spalling resistance is improved due to more flexible structure.

4.4.5 Conclusions

(1) SiC addition in ULC bauxite-based castable specimens has a remarkable impact of improving HMOR at 1400 °C. For A series specimens (ultra fine Al_2O_3 / SiO_2 =75/25), HMOR increases with increase of SiC contents, whereas for S series specimens (ultra fine Al_2O_3 / SiO_2 =25/75), the optimum SiC addition is 4 ~ 8%.

(2) MOR — T curves illustrate that MOR increases with temperature rise at low and medium temperatures up to inflexion point 800 °C or 1000 °C, after which MOR decreases.

(3) The stress-strain behavior of the specimens may be divided into three stages: elastic range from RT to 600°C; "plastic flow range" (600°C~1000 °C) and "viscous flow" range (1000°C and above).

(4) SiC addition is also very effective in improving TSR of castable specimens. With increase of SiC contents, significant increase in residual strength ratio is observed, with maximum values at 4 ~ 8% SiC addition.

(5) The positive effects of SiC addition on HMOR and TSR of bauxite-based castables may be attributed to: (a) SiC possesses lower thermal expansion, higher thermal conductivity and higher strength; (b) SiC crystals are mostly prismatic or elongated and are more resistant to thermal stresses; (c) SiC crystals interlaced into corundum-mullite structure would create a reinforcing effect.

4.4.6 References for chapter 4.4

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[2] M. G. Bassin, S. M. Brodsky, H. Wolkoff, Statics and strength of materials, 3^{th} Edition, McGraw-Hill Book Inc. Press, USA, 1971. 137~155.

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CHAPTER 5. RHEOLOGY OF ULTRA-LOW CEMENT ALUMINA BASED CASTABLES

5.1 SYNTHESIS

This chapter is about alumina instead of bauxite-based castables, but also about ultra-low cement containing castables, without and with graphite. This has been the source of two papers, one already published and the other already accepted.

It was known in CIREP`s laboratory that adding carbon to castables has a detrimental effect on rheological behavior, but no precise and systematic measurements had been completed.

As shown in the previous section, it is important to optimize first the microsilica content, the ultra fine alumina to silica ratio, and also all the particle size distribution of the mixes. This part of the thesis has allowed us to document the effect of the nature of the graphite being added, flake graphite versus extruded graphite pellets (prepared at CIREP). The end results are, that to obtain comparable flow values of 200mm, the water content with no carbon addition jump from 4.6% to 9.6% with 5% addition of flake graphite but increase to 6.2 % with 6 % addition of extruded graphite pellets (same carbon content). Under such conditions of water addition, the torque viscosity (in Nm.sec.) of the 3 mixes varies from 1.95 to 1.18 after 10 minutes of mixing and from 2.30 to 1.17 and 1.59 after 40 minutes of mixing, respectively. The yield stress for the 3 mixes, (in Nm.) varies from 0.41 to 2.29 and 0.85 after

10 minutes of mixing and from 0.42 to 2.79 and 1.59 after 40 minutes of mixing. Those are very important results to predict the usefulness of such mixes, in terms of pumpability.

It is important to note that:

- Rheological behavior of the ultra low-cement alumina-based castables with and without graphite follows a Bingham flow pattern.
- The rheological behavior of extruded graphite pellet containing castables is much better than that of flake graphite containing castables under the test conditions with much lower water demand (water content reduced by 34.4 wt %), due to improvements of hydrophilic and dispersion properties of extruded graphite.
- Compared to flake graphite, EG pellet additions result in reduced flow resistance (H) and yield stress (G) for the castables.

5.2 RHEOLOGICAL BEHAVIOR OF ULTRA-LOW CEMENT ALUMINA BASED CASTABLES

This is the title of a paper which has been published in "INTERCERAM", Germany, Vol.53, No.1, 2004, 8 ~ 12.

5.2.1 Abstract

Rheological behavior of castables is a very important property for predicting the workability of high-performance castables, such as pumping and shotcreting castables. In this work, rheological behavior of ultra-low cement fused alumina castables has been studied

employing IBB rheometer V1.0 to measure torque (shear stress) as a function of shear rate. Effects of ultra fine powders (microsilica and alumina) and particle size distribution (PSD) on rheological behavior have been investigated. Optimum ultra fine powder ratio (alumina/microsilica) and particle size distribution with good rheological properties are recommended.

5.2.2 Introduction

As an innovation of the recent years, the development of highly efficient installation techniques - pumping or shooting (sometimes also described as “wet spraying” or “wet gunning”) of modern castables continues to gain popularity worldwide. During the installation, castables are subjected to action of shearing forces as they move in the transportation hoses at different velocities, and thus their rheological properties become especially important. Not surprisingly, the investigations of the rheology of castables have become a hot topic in monolithic refractories research.

Rheology is defined as the science of the deformation and flow of matter under loads. In refractories, it mainly relates to the plastic deformation and viscous flow of castables. In a vast number of studies, the rheological behaviour of a fluid or suspension is evaluated by its viscosity at different shearing rates. But in the absence of a shearing force acting on the fluid, its viscosity is a measure of fluidity; in this case, fluidity and viscosity are significantly different concepts.

In this work, the rheological behavior of ultra-low cement alumina-based castables has been studied employing an IBB rheometer V1.0 which allows measurement of torque (shear stress) of the castables under varying shear rates. The values of both flow resistance and torque viscosity were recorded and the flow curves (torque vs. shear rate) were used to evaluate their rheological behavior, and in particular the influence of ultra-fine silica and alumina powders and particle size distribution.

5.2.3 Experiments

1) Raw materials

The raw materials used for the tests include:

Fused alumina: $Al_2O_3 \geq 98.5\%$, as aggregates (5 ~ 0.088mm) and fines (< 200 mesh, D50 = 42.05μm; < 325 mesh, D50 = 22.91μm).

Calcium aluminate cement: Secar 71, Al_2O_3 69.0 ~ 72.2 %, CaO 27.0 ~ 30.0 %, D50 = 12 μm.

Microsilica: Elkem 971U, $SiO_2 \geq 97.0$ %, D50=0.51μm.

Ultra-fine alumina: $Al_2O_3 \geq 98.5$ %, (< 4.0μm, D50 =1.8μm).

2) Preparation of specimens

According to Andreasen's particle size distribution model, an approximate q value of 0.29 is used for design of particle size distribution of the castables. Two groups of specimens of fused alumina-based castables with 2 wt% of cement were prepared: one group with varying ultra-fine alumina/ microsilica ratio (i.e. Al_2O_3 / SiO_2 = 0/100, 25/75, 50/50, 75/25 and 100/0, while keeping the total amount of two ultra fines at 8%) – to study the influence of ultra-fine powders on rheological behavior of the castables; the other group - with fixed ultra-fine alumina/ microsilica ratio 50/50 (i.e. 4 % ultra-fine alumina and 4% microsilica), and different q values (0.29, 0.26 and 0.23) – to study the effect of particle size distribution on rheological properties.

For each rheological test, a 10-kg castable mix was uniformly mixed and then thoroughly blended using a two-step added water method (4.3 ~ 5.8% water addition).

3) Experimental method

Immediately after wet blending, self-flowing value of the castable mix were measured using circular cone as described in ASTM-C1445-99.

The IBB rheometer (1) which has been used in this study, consists of a sample bowl and 3/4 HP motor that drives an H shape impeller in a planetary motion. A tachometer provides speed input and a torque meter provides torque input to a computer. The torque imposed is increased in step functions, following one of two possible rates of increase: high and standard. By recording torque at different impeller speeds it is possible to represent the rheological behavior of castables. With proper treatment and analysis, the yield stress and shear stress (torque) can be obtained. Finally, the rheological behavior can be expressed by the following equation:

$$T = G + HN \qquad (5\text{—}1)$$

Where, T is the value of torque applied to the impeller (Nm); G is the flow resistance (Nm); H is the torque viscosity (Nm.s) and N is the impeller angular speed (rev/s). The torque stress is a function of shear rate; the flow resistance (G) is related to the yield stress and the torque viscosity is related to the plastic viscosity; Although the G and H values are instrument-dependent properties, by means of proper calibration, they can be used to calculate the yield stress τ_0 (Pa) or plastic viscosity μ (Pa.s), fundamental for castable rheological properties.

For the measurements, the wet-blended castable mix is poured into the bowl of the rheometer and shear stress is applied at 5 minute intervals during 20 and 30 minutes under higher torque rate increase, and at 10 minute intervals during 60 minutes under normal torque rate increase. The resulting curves (torque vs. impeller speed) are used to evaluate rheological behavior of the castables.

5.2.4 RESULTS AND DISCUSSIONS

5.2.4.1 Effects of ultra fine powders on rheological behavior

The effects of ultra fine powders on rheological properties are shown in Fig. 5.2.1 to 5.2.5.

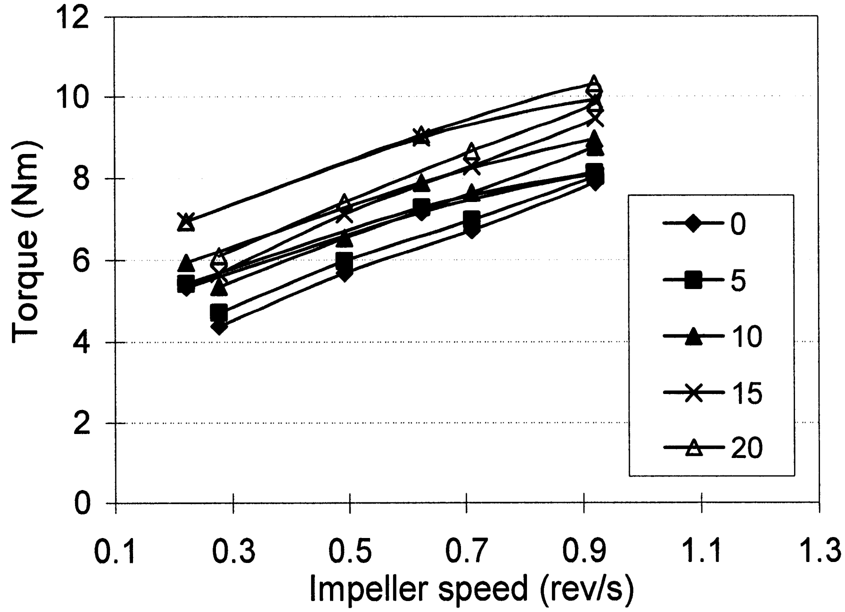


Fig. 5.2.1 Rheological curves of castables with ultra-fine alumina/ microsilica ratio = 100/0

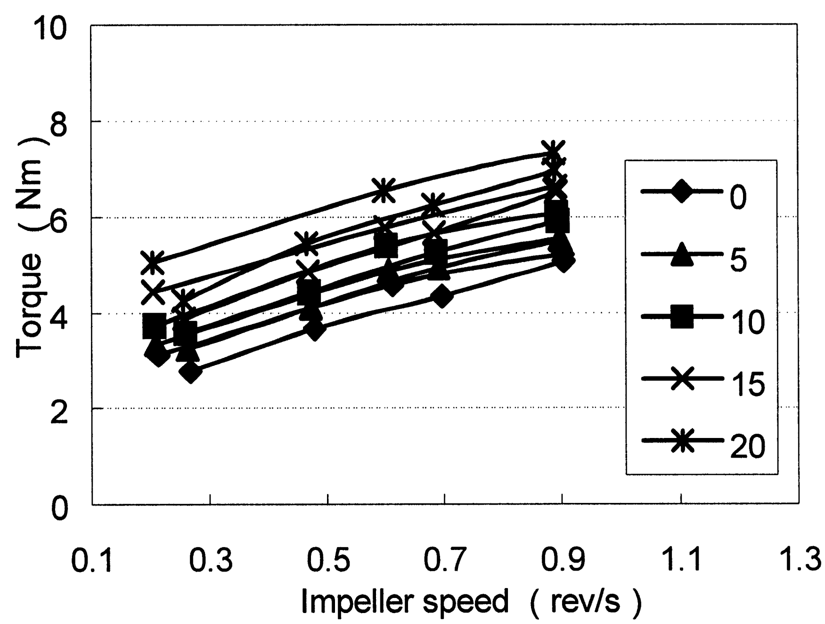


Fig. 5.2.2 Rheological curves of castables with ultra-fine alumina/ microsilica ratio= 75/25

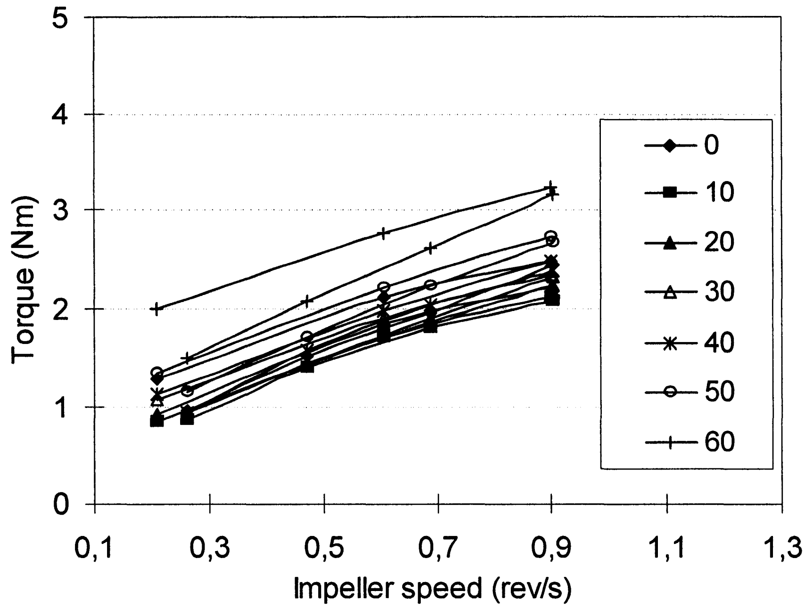


Fig. 5.2.3 Rheological curves of castables with ultra-fine alumina/ microsilica ratio= 50/50

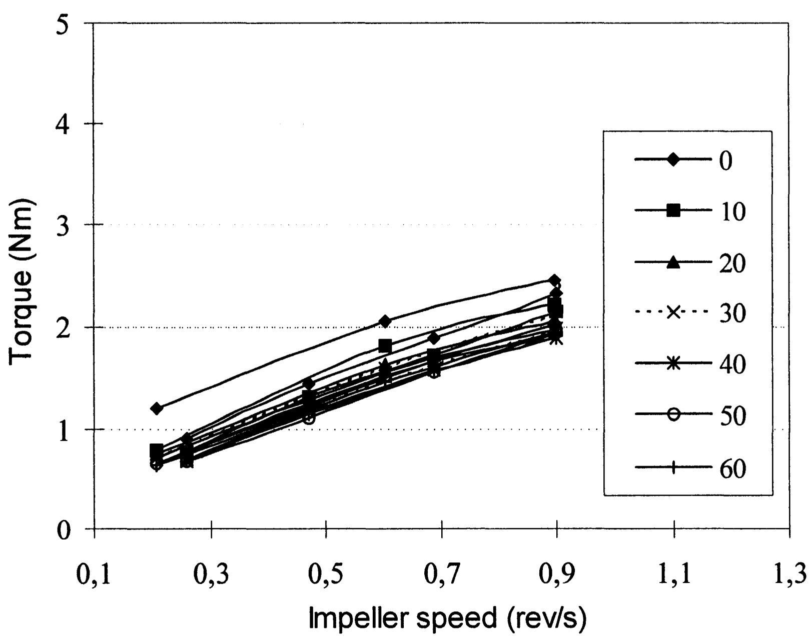


Fig. 5.2.4 Rheological curves of castables with ultra-fine alumina/ microsilica ratio= 25/75

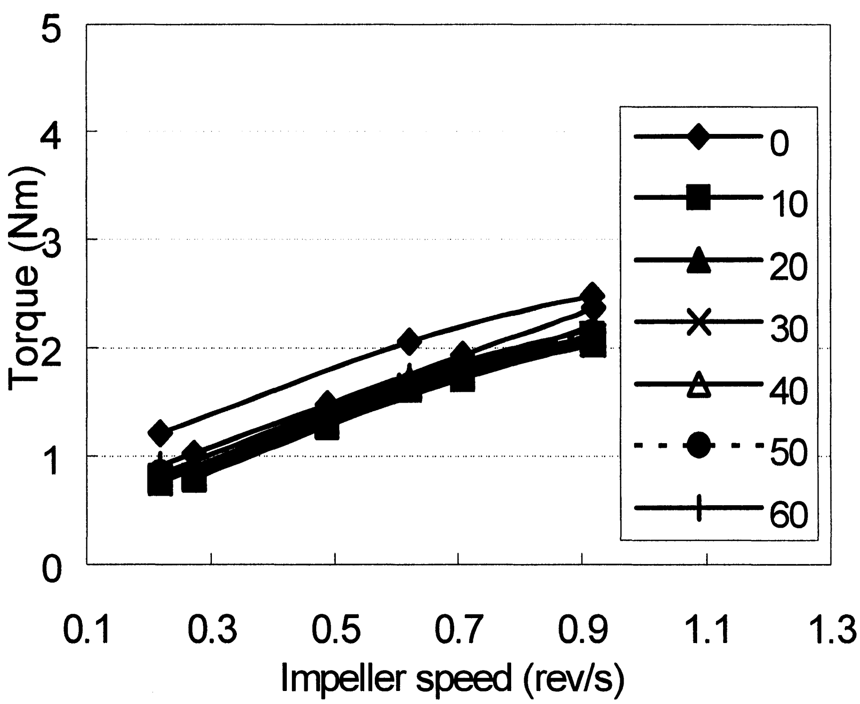


Fig. 5.2.5 Rheological curves of castables with ultra-fine alumina/ microsilica ratio = 0/100

It can be seen from the above figures that the flow curves follow a Bingham flow pattern.

(1) When two ultra fine powders (alumina and silica) with different ratios are used simultaneously in the ultra low-cement alumina castables, the decrease of ultra fine alumina/microsilica ratio (i.e reduced content of ultra fine alumina) leads to the decrease in torque and yield stress, meaning an overall improvement of the rheological properties. The samples with high contents of ultra fine alumina exhibit relatively poor rheological behavior with increased amount of water (see fig. 5.2.8).

(2) When alumina/microsilica ratio is over 50:50, the rheological behavior tends to be stable, showing lower torque and yield stress values.

(3) Castable samples with high microsilica content always show lower torque and yield stress values in 60 minute tests, maintaining good rheological behavior long enough for installation. On the other hand, the torque and yield stress of the samples with higher ultra fine alumina content overload the rheometer. Such a sharp increase of viscosity in short time is detrimental to installation of the castables.

In Fig. 5.2.6 and 5.2.7, the variation of the torque viscosity (H values) and flow resistance (G values) of samples tested for 60 minutes are shown. In accordance with the previously mentioned results, the samples with higher microsilica content always have lower torque viscosity and flow resistance values during 60 minute tests, whereas the samples with higher ultra fine alumina content show noticeably high plastic viscosity and flow resistance values. Overall, when microsilica contents in ultra fine alumina/microsilica ratio is ≥50% (i.e. ≥4% of the total weight), their rheological parameters (torque, yield stress, torque viscosity and flow resistance) are stable, leading to satisfactory rheological properties.

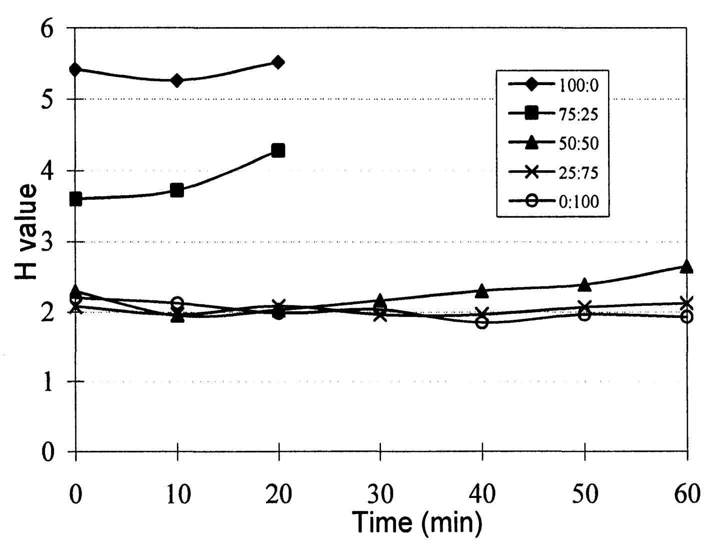


Fig. 5.2.6 Torque viscosity (H) dependence on time

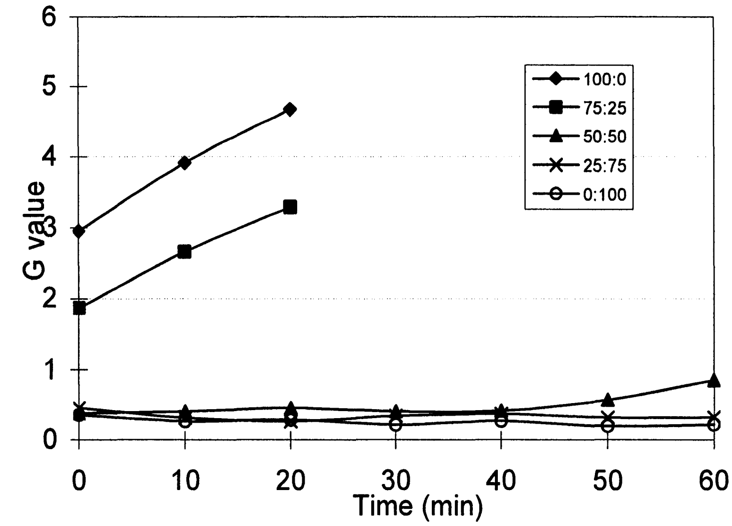
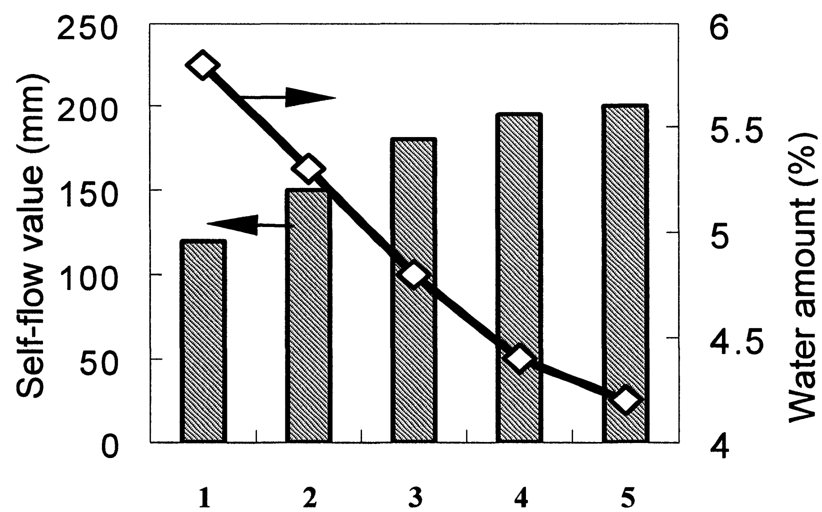


Fig. 5.2.7 Flow resistance (G) dependence on time



Sample Code*

Fig. 5.2.8 Self-flow value vs water amount of the samples with different ratio of ultra fine powders *(*The sample code 1 to 5 express ultra fine alumina/ microsilica ratio from 100/0, 75/25, 50/50, 25/75 and 0/100 respectively)*

The relationship between self-flow values, amount of added water and alumina /microsilica ratio is shown in Fig. 5.2.8.

It is seen from Fig.5.2.8 that the sample 1 containing ultra fine alumina, but no microsilica exhibits the highest amount of added water (5.8%), and the lowest self-flow value (125mm); the sample 3 with alumina/microsilica ratio 50/50 required 4.8 % of water and has a self- flow value of 180mm. These results indicate that microsilica reduces remarkably the water amount needed for casting and improves the flowability of the castables.

As rheological characterization and self- flow value of the castables are put together to evaluate workability of modern castables, it may be concluded from the above results that in ultra low cement alumina castables, microsilica addition improves significantly rheological properties and assures adequate working time. Its contribution to improvement of rheological properties is greater than that of ultra fine alumina addition.

The beneficial effect of microsilica is related to its submicron particle size and globular morphology. By using a suitable dispersing agent, microsilica particles can be dispersed uniformly in the microstructure of castables. When microsilica powder is added to the castable, it fills small pores and displaces some of the water present in the voids. Thus the flocculated structure in the castable matrix is disrupted and the water in fillers is released, resulting in better dispersion of particles in the matrix. At the same time, because of the gradual ionization on the surface of the SiO_2 particle in contact with water [2], $Si\text{-}O^{-}+H^{+}$ sol is formed from dissolving Si-OH base (silanol base) on the surface of the ball shaped microsilica particles and this has a good lubricating effect on the particles in the matrix. So, yield stress, torque and plastic viscosity of the castables are decreased, rheological behavior is considerably improved; water amount for forming samples is decreased, flowability is increased and work time is substantially extended. Previous research on the influence of super-fines in high alumina castables also shows that both microsilica and ultra fine alumina may act as fillers. However, the microsilica is much more effective in terms of flowability and may provide by itself the highest flow values of castables [3].

Considering the alumina castables properties at high temperatures, the optimal ultra fine alumina/microsilica ratio of 50/50 or 25/75 is recommended in line with another report [4] which signaled that alumina castable samples with alumina/ microsilica ratio of 30/70 yielded best placement and dried properties, together with acceptable hot properties. This ratio is therefore considered to be optimal for overall properties.

5.2.4.2 Effects of particle size distribution (PSD) on rheological behavior

Particle packing theories most used in refractory castables are based on Andreassen, Furnas and Dinger-Funk equations. The PSD equations are according to:

Andreassen: $$CPFT / 100 = (D/D_L)^q \qquad (5—2)$$

Furnas: $$CPFT / 100 = (r^{\log D} - r^{\log Ds}) / (r^{\log L} - r^{\log Ds}) \qquad (5—3)$$

Dinger-Funk: $$CPFT / 100 = (D^q - Ds^q) / (D_L^q - Ds^q) \qquad (5—4)$$

Where D — designed particle size; D_L — largest size; D_S — smallest size; q — PSD coefficient; r — ratio of particles between two adjacent sieves; CPFT — cumulative volume percent finer than.

The Andreassen's equation is most widely used to PSD design of castables as it places no limit on the smallest particle size [5].

In this work, to meet different requirements of installation methods---vibrating, self-flowing and pumping, three particle size compositions with different q values (0.29, 0.26 and 0.23) were selected for studying the effects of particle-size distribution on rheological behavior of castables. Their rheological results are shown in Fig. 5.2.9 to 5.2.11.

Relationship between the torque viscosity (H values) and flow resistance (G values) of castable samples with different q values tested within 30 minutes are shown in Fig. 5.2.12 and 5.2.13. The relationships among self-flow value, water amount of the castables and different q values of particle size distribution are shown in Fig. 5.2.14.

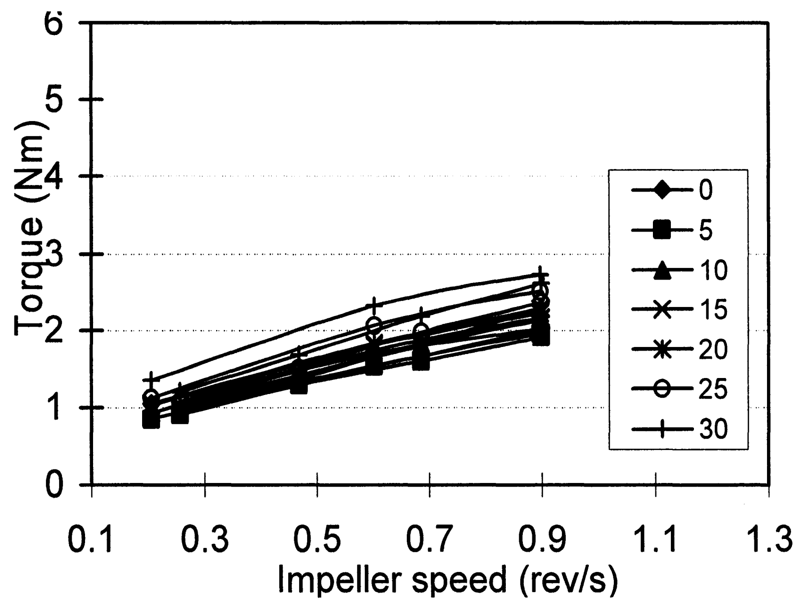


Fig. 5.2.9 Rheological curves of castables with PSD of **q=0.29**

(* Data of this figure is from Fig.5.2.3)

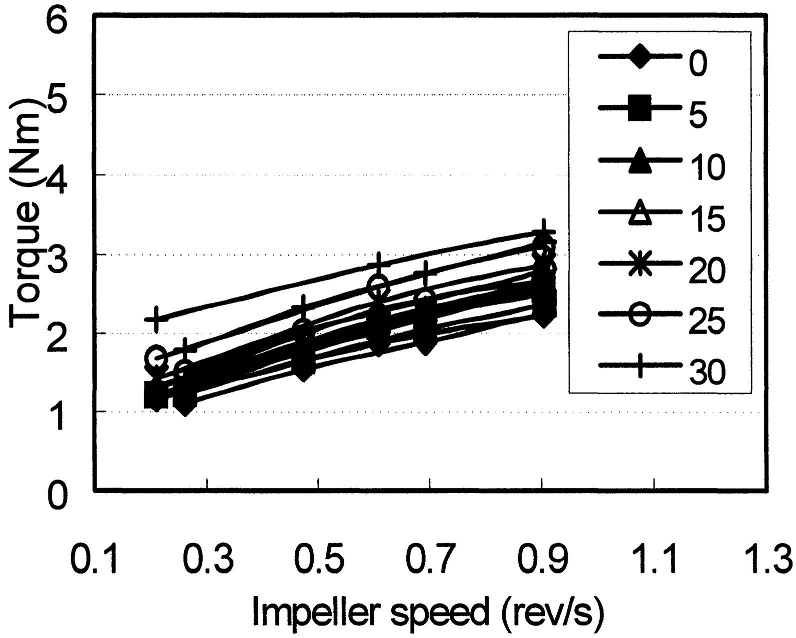


Fig.5.2.10. Rheological curves of castables with PSD of **q=0.26**

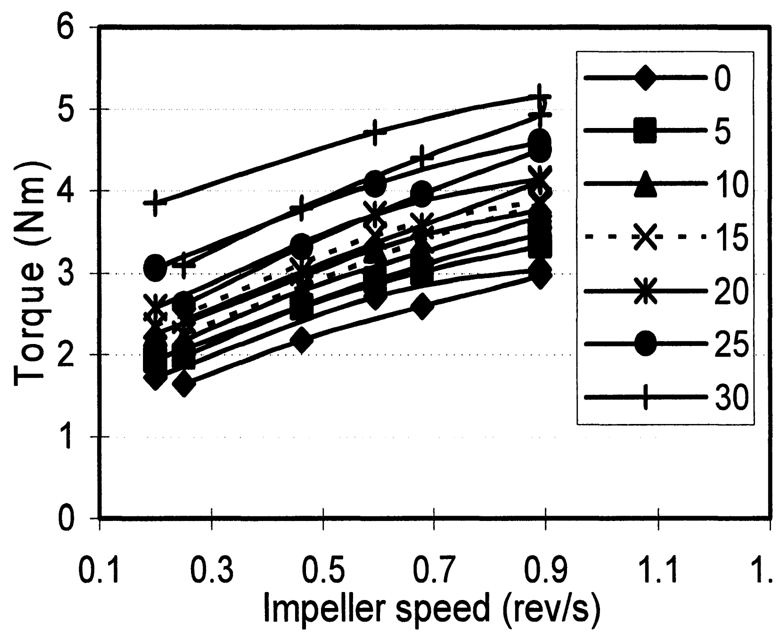


Fig.5.2.11. Rheological curves of castables with PSD of **q=0.23**

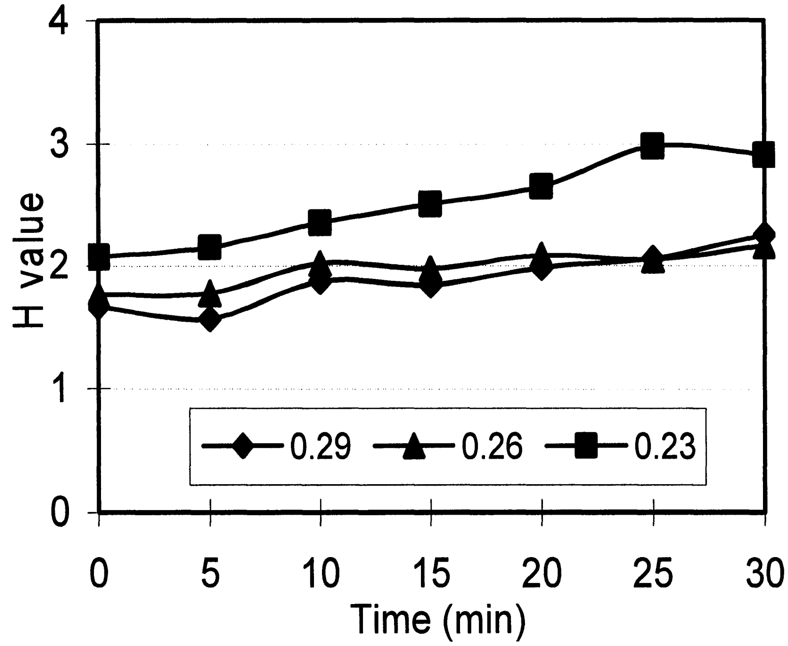


Fig 5.2.12. Plastic viscosity (H) dependence on time

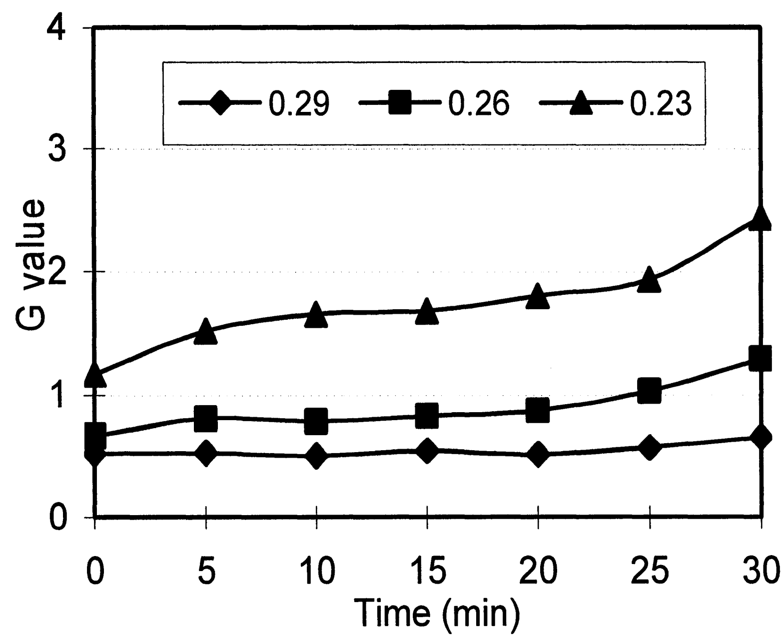


Fig. 5.2.13 Flow resistance (G) dependence on time

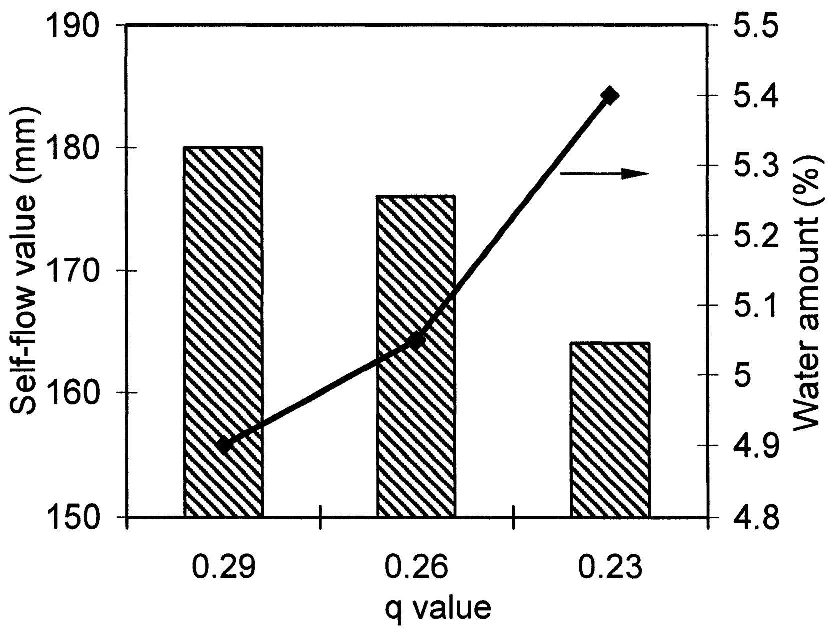


Fig. 5.2.14 Self-flow value vs water amount of the samples with different q values of PSD

It can be seen from Figures 5.2.9 ~ 5.2.14, that the variation of q values from 0.29 to 0.23, while maintaining constant composition and bonding system (ultra fines and cement content), leads to the following:

(1) a decrease of the rheological properties (torque, yield stress) of the castables;

(2) an increase of the torque viscosity (H) and flow resistance (G);

(3) a decrease in flowability (from 182mm to 164mm) even if water amount for the tests increases from 4.9% to 5.4%;

(4) a lower viscosity and flow resistance with elapsed test time, for samples with higher q values .

The results also show that samples with lower q value (i.e. higher filler content) display an increase on yield stress and torque viscosity. This may probably be explained as follows:

with an increase of filler content, surface energy in the system is increased; more contact of particles taken place and the fines tend to agglomerate, to form flocculation structure in the matrix, resulting in an increase of viscosity and shear stress. Therefore, more energy is needed to produce shear in the tests. As shown previously [6], rheological properties are adversely affected if the content of fine particles is excessive.

5.2.4.3 Improvement of rheological behavior of the castable with PSD q= 0.23

In application of Andreasen's PSD pattern, normally, 90% of particle size composition given from q value is identical with the PSD of practical castables showing PSD of coarse grains and powders, but not showing composition portion of <1 micron particles. In other words, q value is not changed by small variation of the amount of < 1μ micro powders. Therefore, for a fixed q value, improvement of rheological behavior of castables may be achieved by adjusting micro powder proportion.

It is well-known that PSD with higher q value containing more coarse grains is not suitable for wet-shotcreting due to higher rebound in spraying placement. PSD with lower q value is better for pumping or shotcreting castables. To maintain lower q value (0.23) and obtain good rheological behavior, we changed the proportion of ultra fine portion in the matrix, by introducing 2 % microsilica in replacement of 2 % alumina powder originally used. Under the test conditions at 5 minutes intervals for 45 minute test duration, the resulting improvement of rheological behavior is shown in Fig. 5.2.15.

Comparing Fig.5.2.11and Fig.5.2.15 for specimens with the same q value (0.23), the later with addition of 2% microsilica displays distinctly superior rheological behavior (lower torque and yield stress). At the same time, torque viscosity (H) and flow resistance (G) are reduced by 33 % and 55% respectively; self-flow value increases from 164mm to 189mm while added water amount varies from 5.4% to 5.0%. It may be concluded from the above that for castables with fixed bonding system, PSD strongly affects its rheological properties; for castables with a fixed q value, an increase of microsilica content considerably improves rheological behavior.

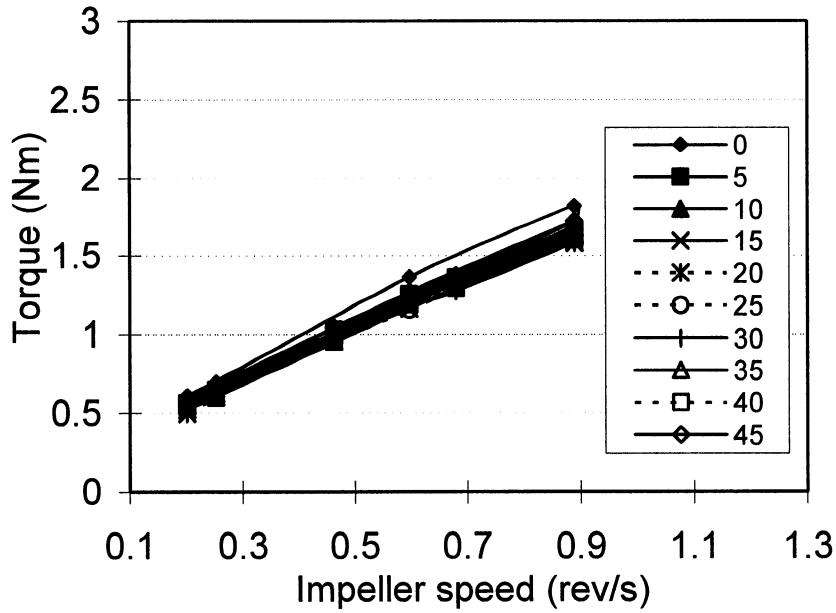


Fig 5.2.15 Rheological curves of castables with **q=0.23** after improvement.

5.2.5 Conclusions

1. Rheological behavior of the ultra low-cement fused alumina castables follows a Bingham flow pattern.
2. When ultra fine alumina and microsilica additions are used together in the castables, an

increase in microsilica content would lead to significant improvement of rheological properties of the castables. Microsilica is thought to be the controlling factor affecting the rheological properties.

3. When ultra fine alumina/microsilica ratio is higher than 50:50, rheological properties tend to degrade, showing higher torque and yield stress values. In order to achieve satisfactory high- temperature properties, ultra fine alumina/ microsilica ratio is recommended to be between a 50/50 to 25/75 ratio.
4. Microsilica addition helps to achieve good flowability and to assure adequate working times.
5. PSD strongly affects rheological behavior of castables. For castables with a fixed lower q value, its rheological behavior can be considerably improved by adjusting microsilica content.

5.2.6 References for chapter 5.2

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5.3 RHEOLOGY OF ALUMINA-BASED GRAGHITE-CONTAINING CASTABLES

This paper has been submitted and accepted for publication in the 4^{TH} International Symposium on Advances In Refractories for the Metallurgical Industries proceedings, Hamilton, Canada, in August 2004, Publisher, The Canadian Institute of Mining and Metallurgy, Materials, Canada.

5.3.1 Abstract

In this work, the rheological behavior of ultra-low cement alumina-based castables with addition of flake graphite and extruded graphite pellets has been investigated by using IBB rheometer. Emphasis has been laid on the influence of the type and amount of carbon addition on rheological properties of the alumina-based castables and the results are compared with corresponding alumina castable samples without any carbon addition. It is found that alumina-based castables with extruded graphite pellets have good rheological behavior and flowability with lower water demand (< 6.3%) and no segregation during the shearing of castable.

5.3.2 Introduction

Carbon –bonded refractories have been developed very fast in the past two decades and more and widely used in steel making and continuous casting processes. Alumina-carbon high performance castables have good prospects in applications as functional monolithic refractories. Now, the functional refractories for continuous casting process of steel making, such as long nozzle, submerged entry nozzles and stopper-monoblock, are a class of high performance monolithic materials made by high technology. To meet the requirement of application, they must possess superior performance to resist the harsh service conditions (such as erosion by molten steel over 1600°C, corrosion by slag, thermal shock from cycling vessels. This type of functional refractories is mostly composed of alumina-carbon monolithic materials with 15 ~ 30% carbon contents, formed by isostatic pressure. However, the application of these refractories with high carbon content has a problem, i.e. the carbon in refractories at high temperatures enter possibly to molten steel, resulting in an increase of carbon in steel and affecting steel quality, especially, when they are used for producing high quality steel (such as ultra-low carbon steel or cleaning type steel). Therefore, the need for lower carbon containing refractories offers an opportunity for development of carbon containing castables and application in continuous casting process.

As carbon sources for refractories, there are many choices (flake or grain graphite, coke, pitch, carbon black etc.). It has been proven that the best choice is flake graphite which compared with other carbon sources, exhibits excellent properties in refractories due to its high purity, perfect crystallization, good oxidation resistance, and superior slag corrosion resistance. Therefore, flake graphite has been used as the prime carbon form for refractory bricks for a many years.

However, the development of carbon-containing castables has met with considerable technical difficulties mainly because incorporating natural graphite into castables is quite difficult owing to its poor wettability, which would lead to dispersion and flowability problems, and thus higher water demand is require for casting. The large difference in density between the graphite and refractory oxide raw materials would lead to segregation. The high porosity caused by higher water demand and lower strength caused by poor bonding between graphite and refractory oxides at elevated temperatures are also important issues to be solved.

Facing these technical difficulties, in recent years, CIREP has carried out much work on developing extruded graphite pellets by modifying properties of flake graphite, by exploring extrusion method and by surface treatments. Many investigations on physical and mechanical properties as well as oxidation resistance and corrosion resistance of carbon containing castables have also been completed or ongoing [(1~4)].

The extruded graphite pellets were found to possess the following advantages [(4)]:

1. Reducing the specific surface area and increasing specific gravity of flake graphite by agglomerating or packaging graphite flakes and refractory oxide together;

2. Upgrading the pellets in terms of densification pore size and oxidation resistance by incorporating suitable antioxidant and oxide fillers inside the pellets;

3. Improving hydrophilic properties of flake graphite and reducing segregation during the castable mixing;

4. Decreasing water demand for mixing castables, thereby reducing porosity of the carbon-containg castable.

In this work, the rheological behavior of ultra-low cement alumina-based castables with flake graphite and extruded graphite pellet addition has been studied by using IBB rheometer.

The tests results are compared with corresponding alumina castable samples without any carbon addition. The influence of the type and amount of graphite addition on rheological properties of the castables have been identified, which should be useful for development of high performance carbon-containing castables.

5.3.3 Experiments

1) Raw materials

The raw materials used for the rheological tests include fused alumina as aggregates and fillers, flake graphite and extruded graphite pellet additions, ultra fine alumina, microsilica (Elkem 971U), and calcium aluminate cement (Secar 71). Their chemical compositions and particle size are shown in Table 5.3.1.

Graphite (EG) pellets used are prepared in CIREP by extrusion method, using mixes of natural flake graphite ($C \geq 97.0\%$, < 0.074mm), refractory oxide and anti-oxidants with a suitable organic binder. After heat treatment, the binder is pyrolized to form carbon bonding in the pellets. Then, surface of the pellets is treated with an organic agent to improve their hydrophilic properties. Subsequently, they are crushed and sieved into different particle size [(4)].

Table 5.3.1 Compositions and particle size of raw materials

Raw materials	Composition and properties
Fused alumina	$Al_2O_3 \geq 98.5\%$, 5 ~ 0.088mm, < 0.074mm, D50 = 42.05μm < 0.044mm, D50 = 22.91μm
Flake graphite	C ≥ 96.0%, < 0.088mm
Extruded graphite pellets	C ≥ 85.0%, 1~4mm, Φ <1mm
CA cement (Secar 71)	Al_2O_3 69.0~72.2 % CaO 27.0~30.0%, D50 =12.0μm
Microsilica	$SiO_2 \geq 97.0\%$, < 1.2μm, D50=0.51μm
Ultra-fine alumina	$Al_2O_3 \geq 98.5$ %, < 4.0μm, D50 =1.8μm

2) Preparation of mixes

According to previous results [5] of rheological properties of matrixes, ratio 1:1 of the two particle sizes (< 0.074mm and < 0.044mm) of fused alumina as filler were respectively selected for the castable mixes. Ratio of coarse grains and matrix portion fused alumina was 62:38. According to Andreasen's particle size distribution pattern, an approximate q value of 0.29 was used for design of particle size composition of the castable samples. Two groups of samples of alumina based carbon-containing castables with 2% cement and with a fixed ratio

(50/50) of ultra-fine alumina/ microsilica (8% of the total amount of two ultra fines) were prepared:

(1) With different contents of flake graphite (2, 4 and 5%) to investigate the influence of natural flake graphite on rheological behavior of the castables.

(2) With different contents of extruded graphite pellets (2, 4 and 6%) to investigate the influence of graphite pellets after modified properties on the rheological behavior.

For each rheological test, a 10kg castable mix made from the above composition was uniformly mixed and then well blended with water and wetting agent. The time for wet mixing is controlled at 4 minutes and each cycle duration of the rheological measurement is automatically fixed by computer control for 80 seconds.

3) Experimental method

The IBB rheometer [6] is used for the measurements of rheological parameters. Before the measurements, vibrated flow-value of the wet blended castable mix is first measured. In the tests, wet castable mix is poured into a bowl of IBB rheometer and torque with varying speed is given at 5 minute intervals for 40 minute test durations for flake graphite containing samples and for 45 minute test duration for the graphite pellets samples. From this, rheological curves (torque vs. impeller speed, i.e. shear stress vs. shear rate, yield stress, variation of torque viscosity with time and flow resistance with time) are obtained to evaluate rheological behavior of the castables with different carbon sources and different contents.

5.3.4 RESULTS AND DISCUSSIONS

5.3.4.1 Rheological properties of alumina-based castables with flake graphite addition

To compare rheological behavior of the alumina-based castables with different contents of flake graphite (2 %, 4 % and 5% by weight), in the tests, a similar level of vibrated flow-value (200 ~ 210mm) is controlled by changing amount of water addition (from 4.6 % to 9.6%). The rheological results of the castable samples are shown in Fig. 5.3.1 to 5.3.7, among them, Fig. 5.3.2 as reference shows the results of sample without any graphite.

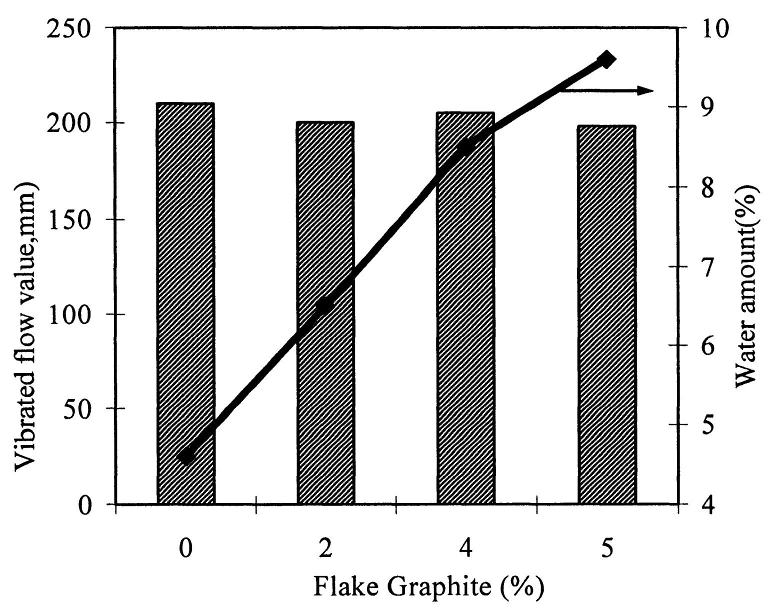

Fig. 5.3.1 Vibrated flow-value vs water amount of the samples with various flake graphite contents

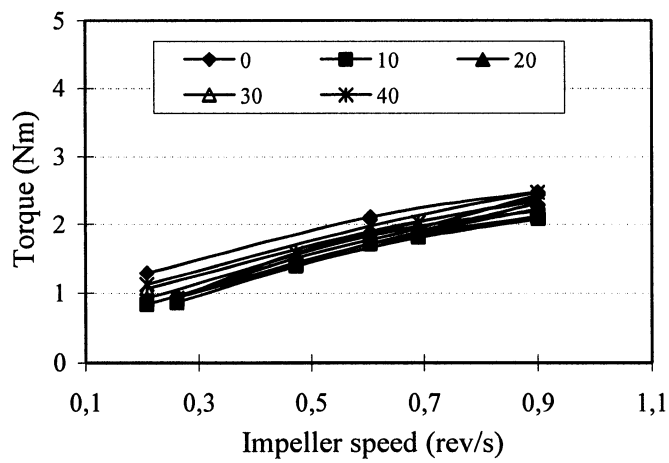

Fig. 5.3.2 Rheological curves of castables without any graphite (4.6 % water)

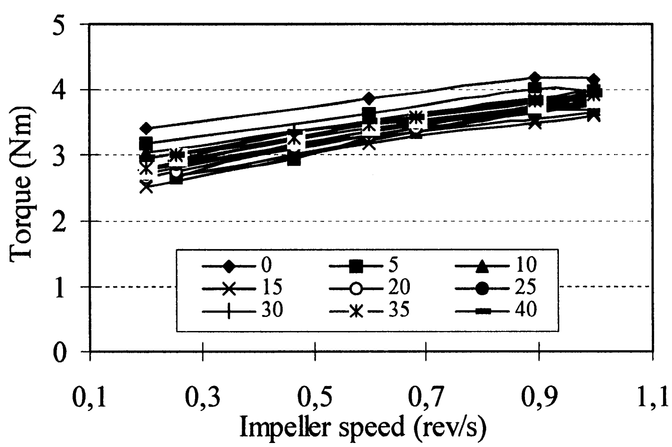

Fig. 5.3.3 Rheological curves of castables with 2 % flake graphite (6.5 % water)

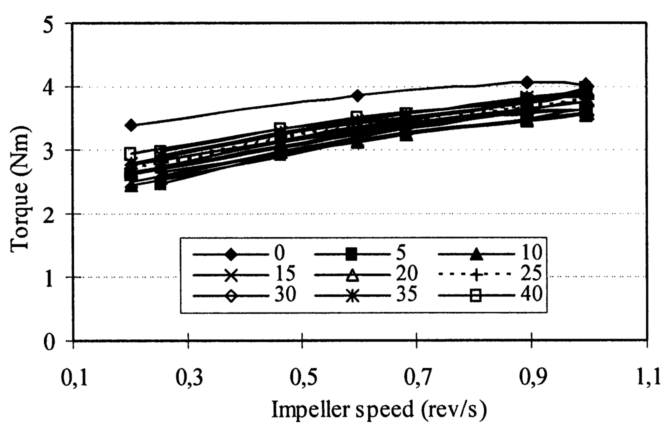

Fig. 5.3.4 Rheological curves of castables with 4 % flake graphite (8.5 % water)

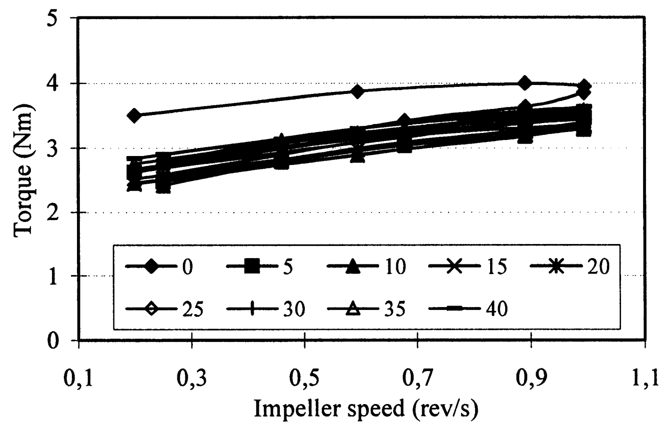

Fig. 5.3.5 Rheological curves of castables with 5% flake graphite (9.6 % water)

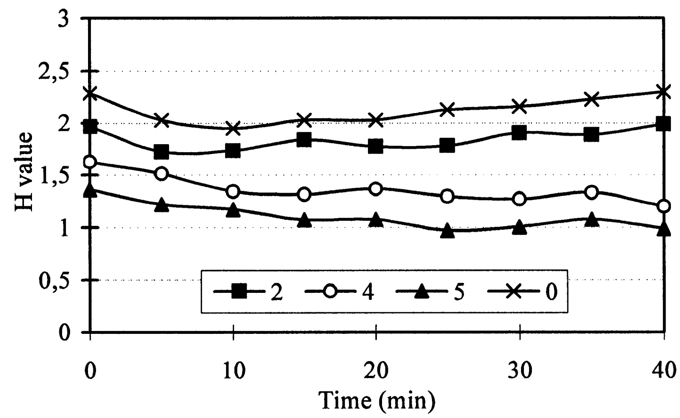

Fig. 5.3.6 Torque viscosity (H) vs testing time of the samples with different flake graphite contents

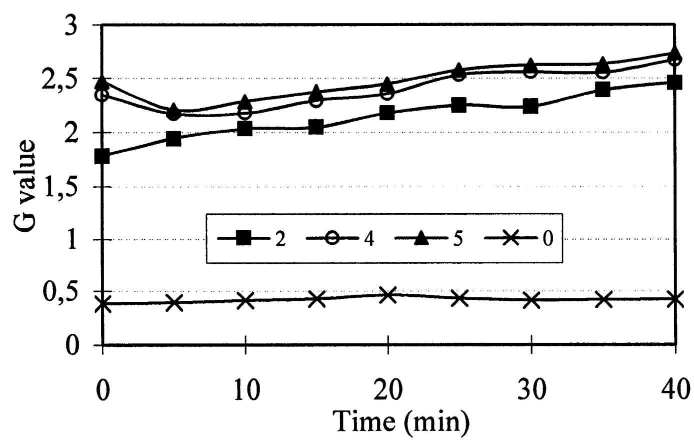

Fig. 5.3.7 Flow resistance (G) vs testing time of the samples with different flake graphite contents

From the above rheological diagrams it can be seen:

(1) The flowability of flake graphite containing castables tends to be deteriorated due to effect of flake graphite addition even when very high water amount is added.

(2) After the first cycle of shearing tests, the structure of the castables tends to be homogenized. The change of shear torque is very little within 40 minutes. All specimens indicate Bingham fluid characteristics and shear thinning within 10 minutes and then slowly shear thickening.

(3) The rheological behavior of the alumina- based castables without flake graphite is much better than that of castables with flake graphite, showing low torque, flow resistance and the lowest water demand in shearing.

(4) With increase in flake graphite contents (from 2% to 5%) and corresponding remarkable increase in water content (from 4.6% to 9.6%), their torque and yield stress at varying shear rates are increased, i.e. their rheological properties are remarkably deteriorated.

(5) During 40 minute testing time, torque viscosity values (H) of the castable sample with 0 and 2 wt% flake graphite exhibit slight rise with elapse of testing time, whereas H of the castable sample with 4% and 5% flake graphite shows slight decrease with testing time. All samples with flake graphite have higher flow resistance (G), which increases with time elapse.

The degradation in rheological properties of flake graphite containing castables is due to the two main drawbacks of graphite:

- Poor wettability by water, leading to dispersion and flowability difficulties; thus high water demand is needed.

- The large difference in specific gravity between graphite and refractory oxide, resulting in segregation.

Therefore, flake graphite has noticeably negative effects on rheological properties of castables.

5.3.4.2 Rheological properties of alumina-based castables with extruded graphite pellets

Similar as above, the rheological measurements are carried out under the test condition of fixing the level of vibrated flow-value by varying content of water addition (from 4.6 % to 6.3 wt%). The rheological results of the castable samples with different contents of extruded graphite pellets (2, 4 and 6 wt%) are shown in Figure 5.3.8 to 5.3.13.

These figures clearly indicate that the rheological behavior of castables with EG pellets is much better than that of castables with flake graphite even when water demand for tests is reduced by 34.4 wt% at varying shear rates. Though flow resistance (G) of EG pellets containing castables tends to increase with testing time, but their overall values are much lower than that of castables with flake graphite addition. In summary, comparing the rheological behavior of EG pellets containing castables and others:

Water demand:

No graphite $<$ EG pellets $\ll$ Flake graphite;

Flow values, torque and flow resistance (G):

No graphite $<$ EG pellets $<$ Flake graphite;

The typical rheological parameters of the castables with two types of graphite additions are listed in Table 5.3.2 for comparison.

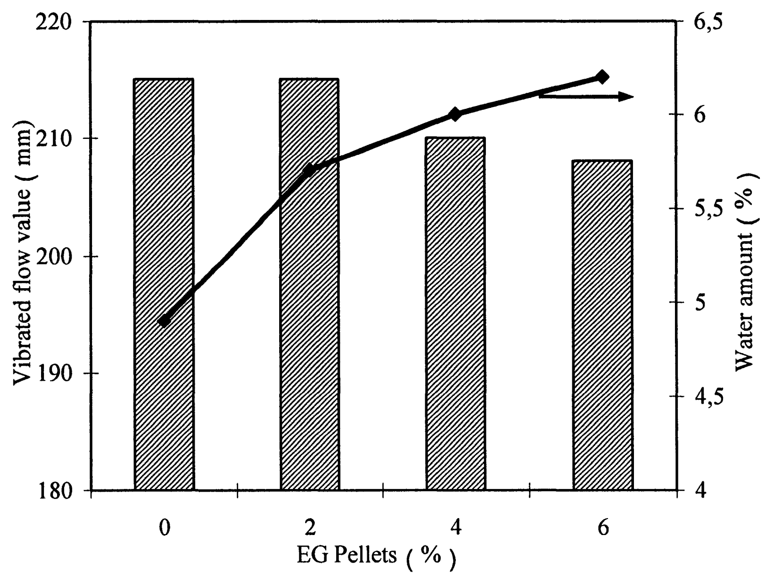

Fig. 5.3.8 Vibrated flow-value vs water amount of the samples with extruded graphite pellets

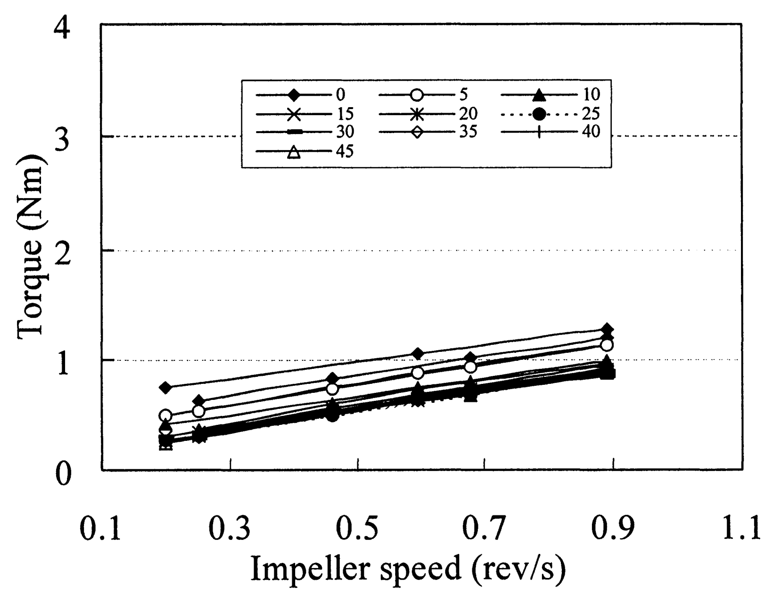

Fig 5.3.9. Rheological curves of the castables with **2%** extruded graphite pellets

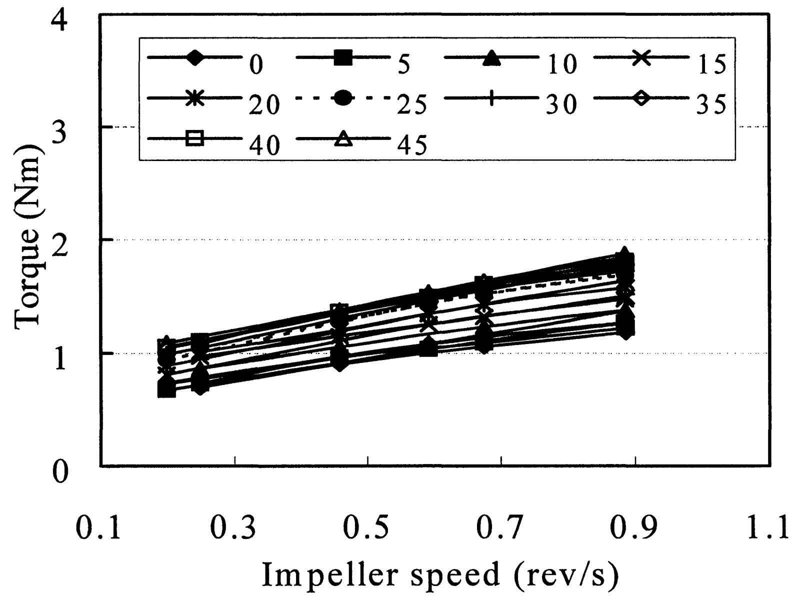

Fig 5.3.10. Rheological curves of the castables with **4%** extruded graphite pellets

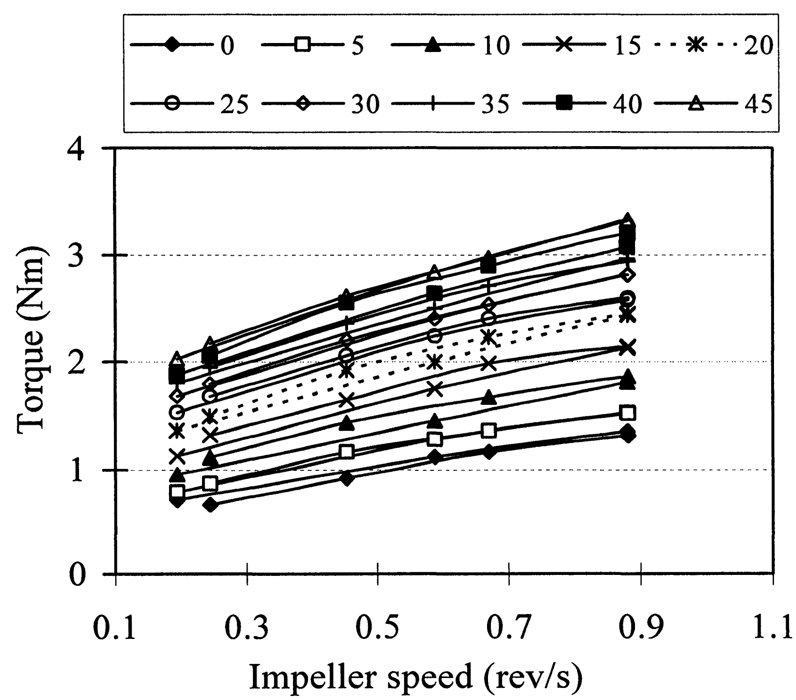

Fig 5.3.11. Rheological curves of the castables with **6%** extruded graphite pellets

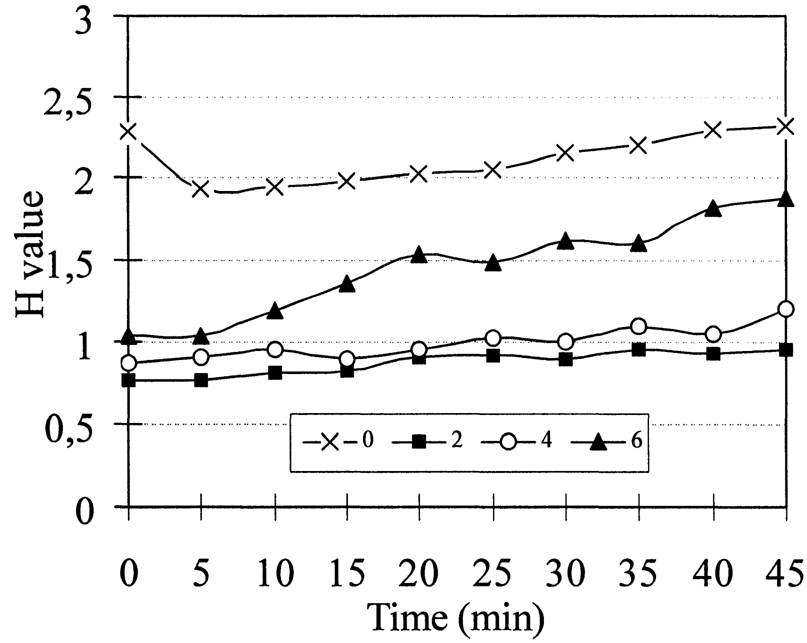

Fig. 5.3.12 Torque viscosity (H) vs testing time of the samples with varying graphite pellets contents

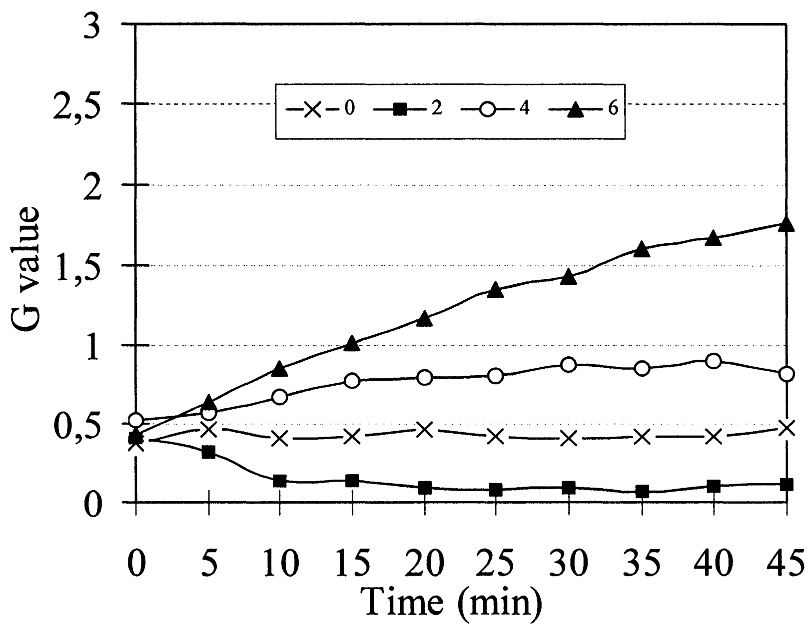

Fig. 5.3.13 Flow resistance (G) vs testing time of the samples with varying graphite pellets contents

The significant improvement of rheological properties of the EG pellets containing castables is because the graphite pellets prepared by extruded method and surface treatment possess improved characteristic in hydrophilic and dispersion properties as well as specific gravity and porosity. Therefore, the EG pellets containing castables may have good prospect for applications as pumpable and shotcreting castables.

Table 5.3.2 Comparison of rheological parameters of castables with different graphite addition

Rheological Parameter	Flake Graphite, (5%)	EG Pellets (6%)	No Graphite
Water, wt%	**9.6**	**6.2**	**4.6**
Flow values, mm	198	208	215
Max. torque*, Nm			
10 minutes	3.33	1.81	2.11
40 minutes	3.63	3.07	2.47
H value, Nm.s			
10 minutes	1.95	1.18	1.95
40 minutes	1.17	1.59	2.30
G value, Nm			
10 minutes	2.29	0.85	0.41
40 minutes	2.74	1.59	0.42

* Under max. impeller speed (= 0.9 rev/s)

5.3.5 Conclusions

The rheological behavior of ultra low cement alumina-based castables with flake graphite and extruded graphite pellets may be summarized as follows:

(1) Both flake graphite and extruded graphite pellets additions have negative effects of different degrees on rheological properties of the castables. But the rheological behavior of extruded graphite pellets containing castables is much better than that of flake graphite containing castables under test condition of much lower water demand (water content reduced by water 34.4 wt%) at varying shear rates. In terms of rheology, the order of merit of carbon additions is: no graphite > EG pellets >> flake graphite.

(2) The better rheological properties of the EG pellet containing castables is due to improvements of properties of hydrophilic and dispersion graphite mixes by extrusion method and surface treatment of EG pellets.

(3) With increase of flake graphite and EG pellet additions and corresponding increase in water content, rheological properties (torque and flow resistance at varying shear rates) of the castables are degraded, the former is much more severe.

(4) There is only little change in rheological behavior with testing time. The rheological behavior of the castable samples tested follows a Bingham flow pattern.

5.3.6 References for chapter 5.3

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CHAPTER 6. RHEOLOGY OF ZERO CEMENT ALUMINA- BASED CASTABLES

6.1 SYNTHESIS

To optimize the high alumina-based magnesia containing castables with graphite, it was decided to tackle the difficulty in two steps:

1) First with no-cement and no-graphite addition, adjusting the microsilica and ultra fine alumina contents with an appropriate PSD, characterized by an Andreasen coefficient of 0.29.
2) Second with graphite pellets (and flake graphite for comparison purpose).

The first paper in this chapter is revealing that with up to 12 wt% magnesia (ball milled magnesia) it is still possible to obtain Bingham fluid characteristics, as in the previous studied castables (chapters 4 and 5). It is possible to compensate for the addition of magnesia by adjusting the microsilica content. At 12% magnesia, the castable mix with 3% microsilica, 6% ultra fine alumina, shows a slight change for rheological properties (increase in torque viscosity with time at a given shearing strain rate). Based on this, varying contents of flake graphite and extruded graphite pellets in alumina-MgO based castable were added. It was found that the alumina-based castable with 8 wt% MgO and 4 ~ 6% extruded graphite pellets have satisfactory rheological behaviour and lower water demand (<6.7%) while no segregation during the shearing was observed.

6.2 RHEOLOGY OF ZERO CEMENT ALUMINA-BASED MgO CONTAINING CASTABLES

This chapter is to be submitted for publication in THE JOURNAL OF THE TECHNICAL ASSOCIATION OF REFRACTORIES, Japan, in May 20, 2004.

6.2.1 Abstract

Alumina-based magnesia containing castables have been widely used for working linings of steel ladles due to their superior hot strength, spalling resistance and corrosion resistance. In this work, rheological properties of zero cement alumina-based MgO containing castables have been studied by means of IBB rheometer V1.0 to measure torque (shear stress) under varying shear rates. Effects of various microsilica and MgO addition on rheological behavior of the castables have been investigated. The results show that with increase in microsilica content (from 1% to 5 wt%) and corresponding decrease in water content, rheological properties at varying shear rates are significantly improved, there is only little change in rheological behavior with variation of ultra fine alumina addition and the castable samples with 4 to 10 wt% MgO contents indicate stable rheological behavior with shear thinning.

6.2.2 Introduction

Alumina-based magnesia containing castables have been extensively used as steel ladle linings because of their superior hot strength, good thermal shock resistance and corrosion resistance. Numerous papers have been published on the alumina-magnesia and alumina-spinel castables, mostly focused on their sintering properties, high temperature properties and their applications, but not much work has been carried out on investigation of their rheological properties, which is of importance, considering MgO addition to castables would lead to short working time and degradation of rheological properties.

An important development in placement methods of refractory castables is the pumping technique which would be very useful in promoting mechanization and automation of installation as well as repairing linings [(1)]. During the pumping process, shearing force between pipelines and castables will be induced. Rheology is defined as the science of studying deformation and flow of matter. For refractories, it mainly discusses the plastic deformation and viscous flow of castables under shearing [(2)]. Therefore, rheological properties of refractory castables have become an important property.

In this work, the rheological properties of zero cement fused alumina-based MgO containing castables has been studied employing an IBB rheometer to measure torque (shear stress) of the castables under varying shear rates (the rheometer has been introduced in previous work [(3)]). The values of flow resistance and torque viscosity are obtained from the rheometer and the flow curves (torque vs. shear rate) are used to evaluate their rheological behavior. In the castables with bonding by MgO-SiO_2-water, effects of microsilica and MgO powder on rheological behavior of the alumina-based castables have been investigated.

6.2.3 Experiments

1) Raw materials

The raw materials used for the tests include:

Fused alumina: $Al_2O_3 \geq 98.5\%$, as aggregates (5 ~ 0.088mm) and fines (< 200 mesh, D50 = 42.05μm; < 325 mesh, D50 = 22.91μm).

Fused magnesia: MgO ≥ 98.5.0%, < 200 mesh, D50 = 40.25μm; < 325 mesh, D50 = 20.0μm).

Microsilica: Elkem 971U, $SiO_2 \geq 97.0\%$, D50=0.51μm.

Ultra-fine alumina: $Al_2O_3 \geq 98.5$ %, (< 4.0μm, D50 =1.8μm).

2) Preparation of mixes

In castable mix specimens, ratio of coarse alumina grains and matrix portion is 62:38. According to Andreasen's particle size distribution model, an approximate q value of 0.29 is used for design of particle size composition of the specimens. Three groups of specimens of alumina based MgO containing castables without cement have been prepared:

(1) With different microsilica contents (1, 3 and 5 wt%) and 8 wt% ultra-fine alumina and 8% MgO addition to study effects of microsilica on rheological behavior of the alumina-MgO castables;

(2) With fixed microsilica content (3 wt%) which is obtained from the testing results of the specimen group one, and 8wt% MgO addition, various ultra-fine alumina contains (4, 6 and 8 wt%) to study effects of ultra-fine alumina on rheological behavior.

(3) With 3% microsilica and 6 wt% ultra-fine alumina contents which is obtained from the

above testing results, and various MgO contents (4, 6, 8, 10 and 12 wt%) to study effects of MgO addition on rheological properties.

From the above composition design, 10kg castable mix for each rheological test is uniformly mixed and then well blended with two-step added water method (5.1~6.0% water addition) for rheological measurements.

3) Experimental method

The IBB rheometer [3] is used for measurement of rheological parameters. Before the measurements, the self-flowing value of the wet blended castable mix is first measured, using circular cone as described in ASTM-C1445-99.

Order of the measurement of rheological parameters was: the wet blended castable mix was poured into the bowl of the IBB rheometer and shear force with varying speed is given at 5 minute intervals for 30 minute test duration for higher torque samples and at 10 minute intervals for 70 minute test duration for the samples with lower torque. From this, rheological curves (torque vs. impeller speed, i.e. shear stress vs. shear rate) are obtained to evaluate rheological behavior of the castables. At the same time, yield stress and shear stress (torque) are provided by the rheometer. Finally, the rheological behavior can be expressed in terms of two parameters obtained from the rheometer by the following equation:

$$T = G + HN \qquad (6\text{—}1)$$

Where, T is the torque to drive the impeller (Nm); G is the flow resistance (Nm); H is the torque viscosity (Nm.s) and N is the impeller angular speed (rev/s). Among them, the flow resistance (G) is related to the yield stress; the torque viscosity is related to plastic viscosity;

The G and H values are influenced by the geometry of the apparatus with that they are measured. Lastly, parameter G and H are converted into the fundamental units of yield stress τ_0 (Pa) or plastic viscosity μ (Pa.s) that are used for evaluation of castable rheological properties as a function of time.

6.2.4 Results and discussions

6.2.4.1 Effects of microsilica on rheological behavior

In zero cement alumina-based MgO containing castables, microsilica is used to form magnesia-silica-hydrate bonding system at room temperature as well as to form mullite at high temperatures. These zero cement bond systems have been developed to a sophisticated level in alumina-based materials, but there are still problems related to rheological behavior must be solved. It is well-known that for reliable application of alumina-magnesia castables with free MgO present in the composition, three inter-linking challenges have to be dealt with: 1) influence of magnesia on castable rheology; 2) risk of magnesia hydration and subsequent disruption of the castable structure; 3) large volume expansion due to reaction with alumina to form spinel which may cause crack formation, high porosity and low strength. To solve these problems, adjusting the content and particle size of MgO addition and the amount of microsilica addition have been found to be effective.

One of main feature of microsilica is its ability to react and form strong bonding strength with MgO at both relatively low and also high temperatures. In the magnesia-silica-hydrate bonded system, the two important factors influencing installation properties of castables (such as rheology, flowability, setting time etc), are microsilica and MgO addition [4]. For investigating the effects of microsilica on rheological properties, rheometer tests of the alumina-based castables with 8 wt% MgO, 8 wt% ultra fine alumina and varying microsilica contents (1, 3 and 5 wt%) have been carried out and their results are shown in Fig. 6.2.1~ 6.2.3. The relationship between self-flow values and amount of added water is shown in Fig. 6.2.4.

From the rheological parameters showing Bingham fluid characteristics, it can be seen that:

(1) In zero cement alumina-based MgO containing castables, with increase in microsilica contents (from 1% to 5%) and corresponding decrease in water content (from 6% to 5.1%), their torque and yield stress values at varying shear rates are noticeably decreased, i.e. their rheological properties are remarkably improved.

(2) The variation of the rheological behavior with time shows shear thickening characteristics, i.e. their torques increase with time.

(3) With elapse of testing time, castable sample with 1% microsilica shows higher torque and yield stress values during shorter testing time (30 minutes), indicating degradation in rheological properties that is detrimental to installation of castables.

(4) The self-flow value of specimens with 1% microsilica is relatively low even when the water content is increased.

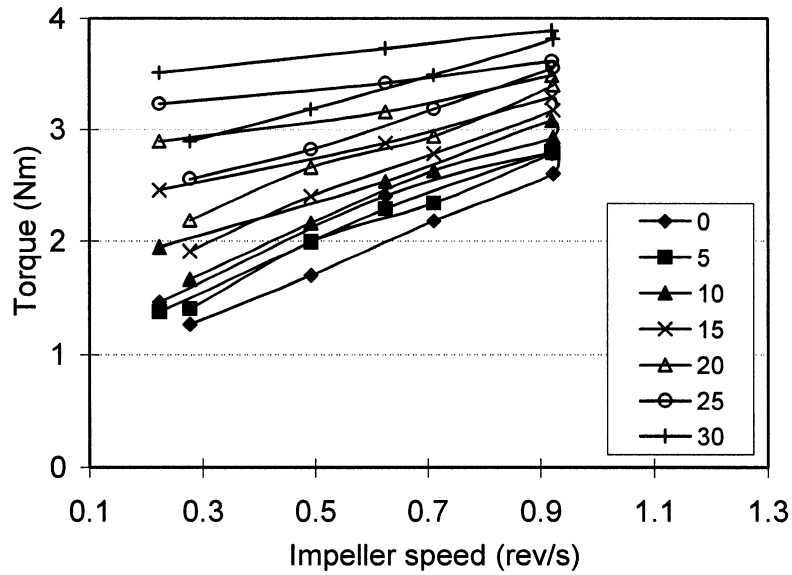

Fig. 6.2.1 Rheological curves of castables with **1%** microsilica and 8 % ultra fine alumina (6% water)

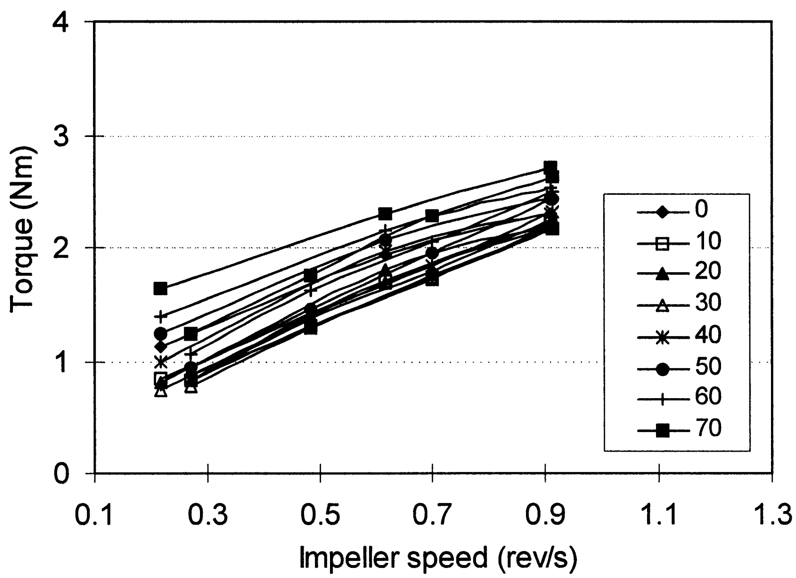

Fig. 6.2.2 Rheological curves of castables with **3%** microsilica and 8 % ultra fine alumina (5.4% water)

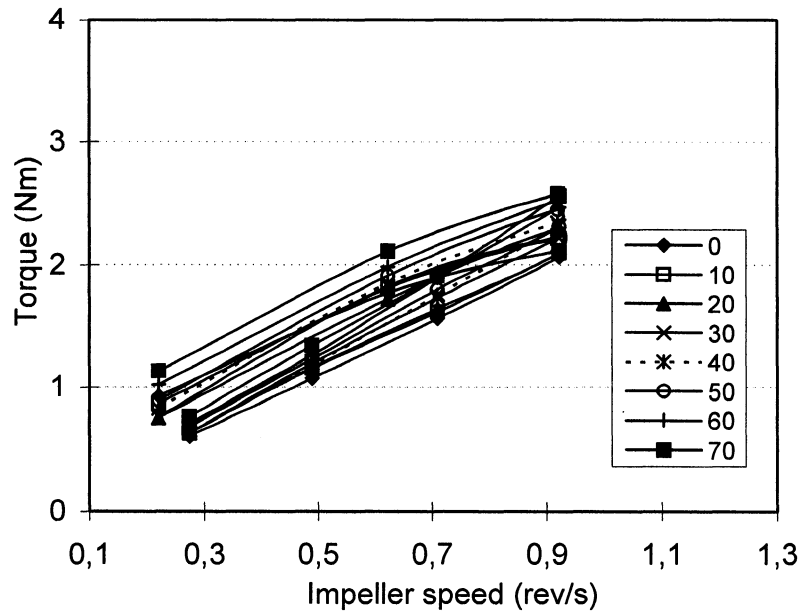

Fig. 6.2.3 Rheological curves of castables with **5%** microsilica and 8 % ultra fine alumina (5.1% water)

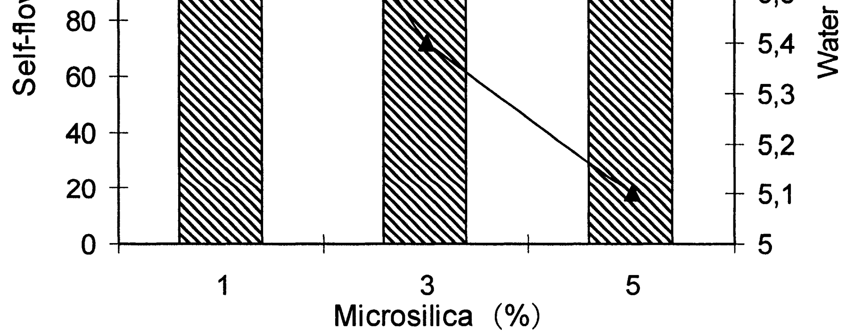

Fig. 6.2.4 Self-flow value vs. water amount of the samples with different microsilica contents

From the results of rheometer, variations of the torque viscosity (H values) and flow resistance (G values) of samples containing different microsilica contents with testing time of 70 minutes have been obtained, which show similar results as above, i.e. the mixes with higher microsilica contents exhibit lower torque viscosity and flow resistance values during 70 minute testing time. The relationship between torque viscosity (H) and testing time of the samples with different microsilica contents is shown in Fig.6.2.5. (The same tendency between flow resistance (G values) and testing time is not shown in here). It is shown that the rheological parameters (torque, yield stress, torque viscosity and flow resistance) of the castables with higher microsilica contents (3% and 5%) are stable, showing satisfactory rheological properties.

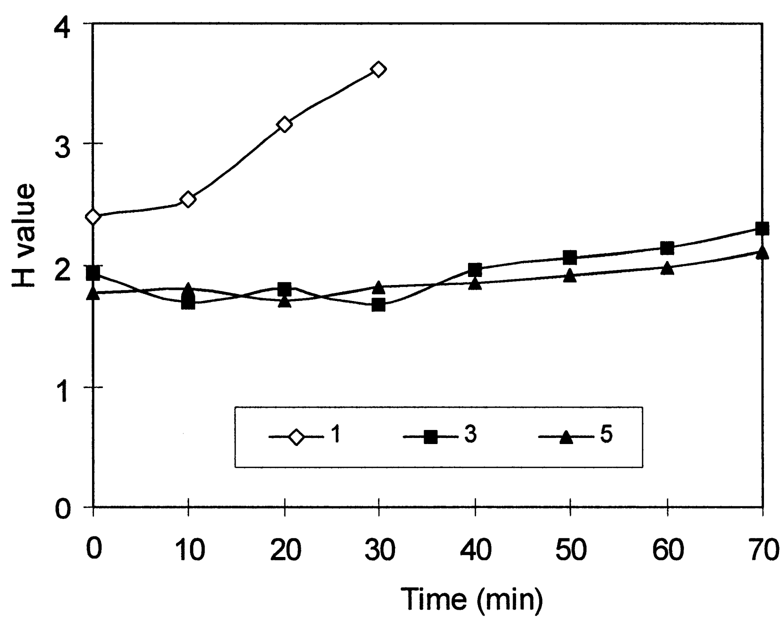

Fig. 6.2.5 Torque viscosity (H) vs testing time of the samples with different microsilica contents

According to rheological testing results and self- flow value of the castables, to evaluate workability of pumping castable or shotcrete, it may be concluded that in the alumina based MgO containing castables without cement, microsilica addition improves significantly rheological properties and also ensures adequate working time. Considering high temperature properties of the castables, optimum microsilica amount of 3% is recommended.

The effect of microsilica on improvement of rheological behavior may be related to its globular morphology and submicron particles size with smooth surfaces. By using suitable dispersing agent, microsilica particles can be dispersed uniformly in the microstructure of castables. When microsilica as fillers is added to castables, it fills into the extremely small pores and displaces the water present in the voids. Thus the flocculation structure in the matrix portion of the castables is disrupted. Consequently, the free water in fillers is released, resulting in better dispersion of particles in the matrix. At the same time, because of gradual ionization on the surface of the SiO_2 particle in contact with water [5], $Si\text{-}O^{-}+H^{+}$ sol is formed from dissolving Si-OH base (silanol base) on the surface of the ball shaped microsilica particles and this has a very good lubricating effect on the particles in the matrix. So, rheological behavior is significantly improved; water amount for casting samples is decreased, flowability is increased and work time is extended.

6.2.4.2 Effects of ultra fine alumina on rheological behavior

Ultra fine alumina with function of filling and auxiliary bonding is used in the alumina-based castables. For investigating the effects of ultra fine alumina on rheological properties of the castables, rheometer tests of the castables with 8 % MgO, 3 % microsilica and varying ultra fine alumina contents (4, 6 and 8 %) have been completed. Higher level of ultra fine alumina addition was not selected for this test because the ultra fine alumina with higher active property react very fast with MgO to form spinel at high temperature, and the reaction results in a large volume expansion which can be detrimental to the castable structure. The rheological results show that there is only little change in rheological behavior with variation of ultra fine alumina contents. (As an example the result can be seen in Figure in front). Based on these results, and at the same time, considering volume expansion caused by spinel formation at high temperature, 6% ultra fine alumina addition was selected for subsequent tests on the effects of MgO addition.

6.2.4.3 Effects of MgO addition on rheological behavior

There have been numerous published papers reporting the superior properties of alumina-based magnesia containing castables. However, for the castables with the MgO-SiO_2-water bond it is sometimes difficult to get sufficient working time for installation [6]. Normally, there are two major problems in the manufacturing process: 1) high MgO content in the castables would lead to short setting time as well as degraded rheological properties; 2) hydration of MgO would lead to formation of cracks in drying and reaction of MgO with Al_2O_3 at high temperature to form spinel would lead to considerable volume expansion. Much research work has been done to solve these problems and some processes and methods have been found for optimizing overall properties. One of the effective methods is the use of MgO powder and microsilica together as binder to form coagulation bonding at room temperature and they react to form forsterite at high temperatures. Rheological behavior of the castables mainly depends on the reactive speed for forming the coagulating bond between MgO and microsilica. Therefore, it is very important to control carefully the reaction between them. To investigate the effects of MgO addition on rheological behavior, microsilica content was fixed at 3 wt% and ultra fine alumina fixed at 6 wt% obtained from the above tests; MgO addition was varied from 4 to 12 wt%, and water demand was kept at the same level for all samples. The rheological characteristics are shown in Fig. 6.2.6 ~ 6.2.10 while the variation of rheological behavior with time is shown in Fig. 6.2.11~ 6.2.12.

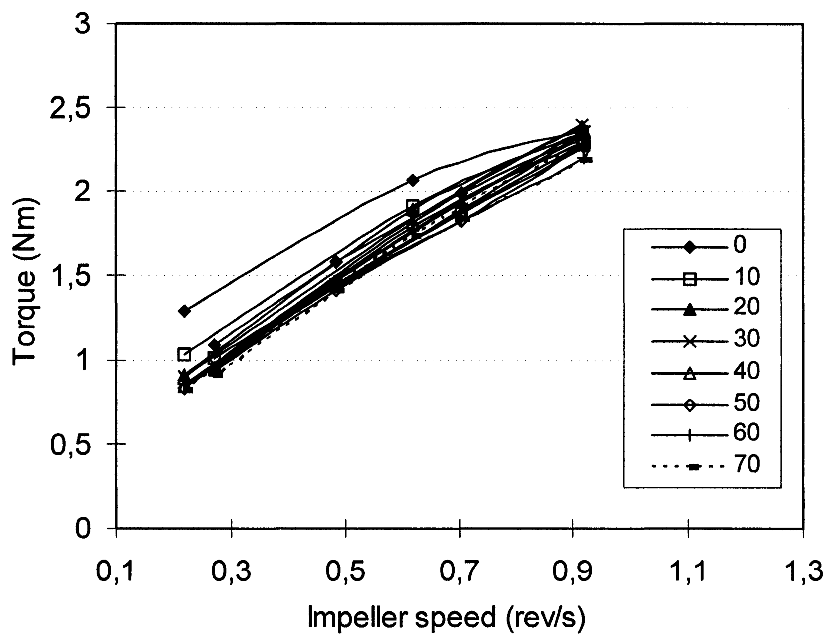

Fig 6.2.6 Rheological curves of the castables with **4%** MgO (3% microsilica and 6% ultra fine alumina)

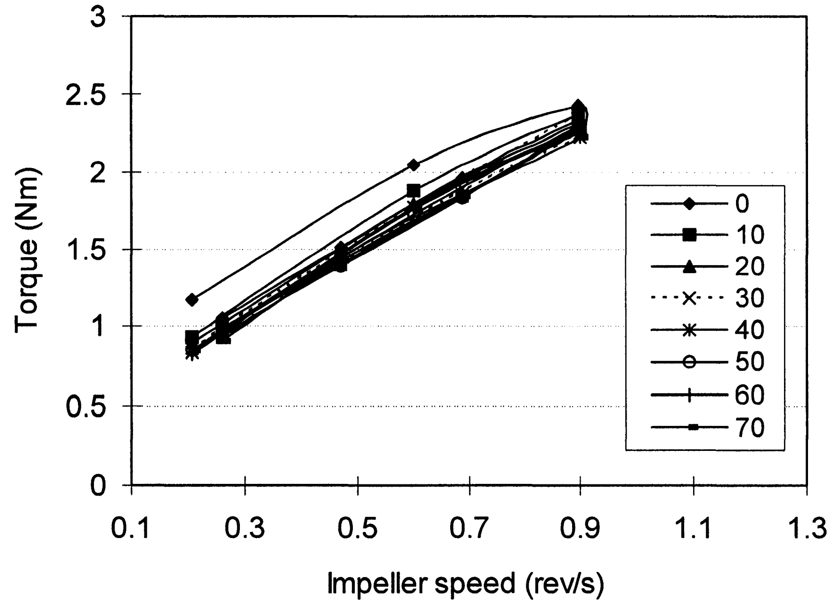

Fig 6.2.7 Rheological curves of the castables with **6%** MgO (3% microsilica and 6% ultra fine alumina)

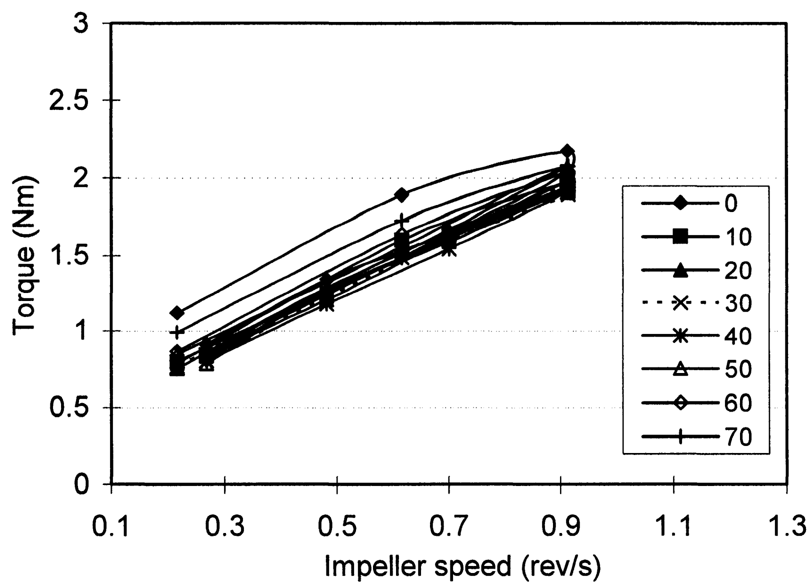

Fig 6.2.8 Rheological curves of the castables with **8%** MgO (3% microsilica and 6% ultra fine alumina)

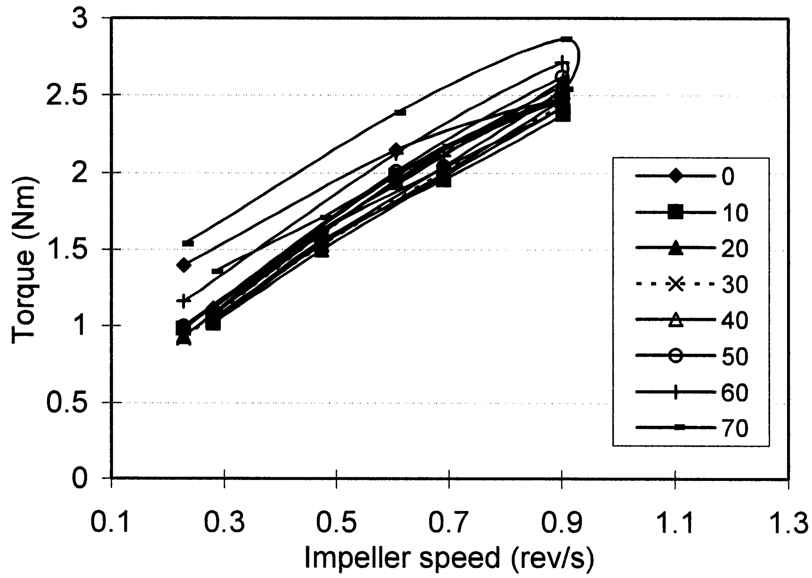

Fig 6.2.9 Rheological curves of the castables with **10%** MgO (3% microsilica and 6% ultra fine alumina)

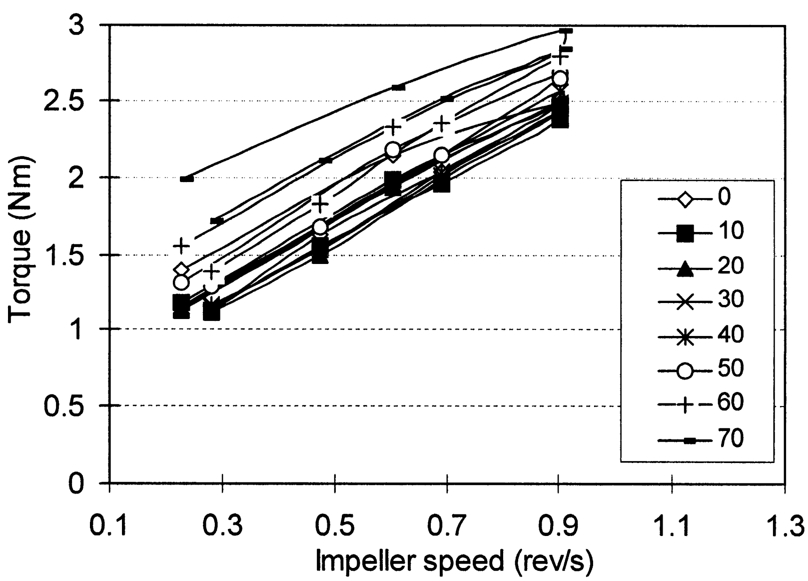

Fig 6.2.10 Rheological curves of the castables with **12%** MgO (3% microsilica and 6% ultra fine alumina)

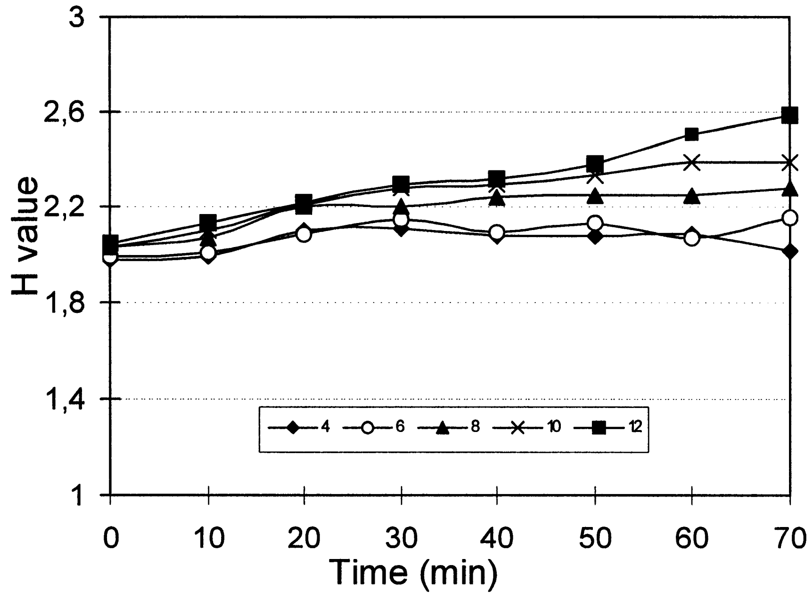

Fig. 6.2.11 Torque viscosity (H) vs testing time of the samples with different MgO contents

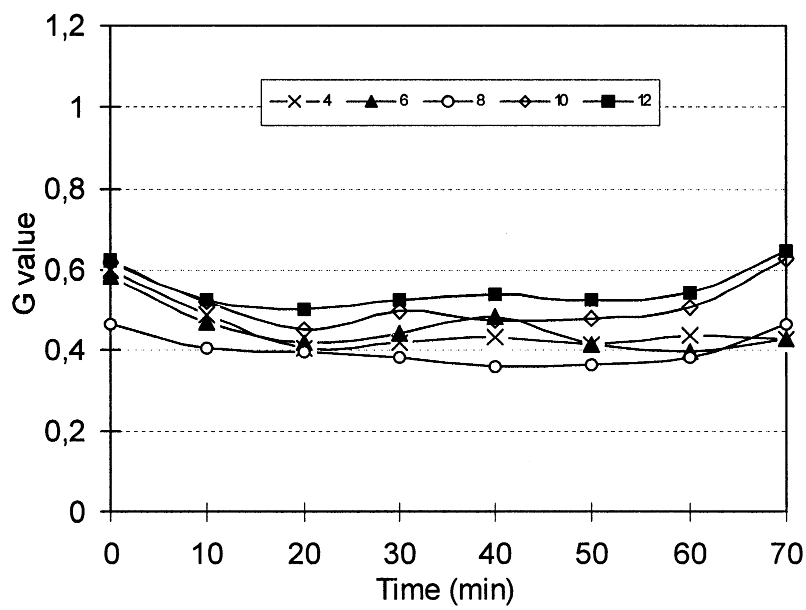

Fig. 6.2.12 Flow resistance (G) vs testing time of the samples with different MgO contents

It is found from Fig. 6.2.6 ~ 6.2.12 that:

(1) Rheological properties (torque, yield stress values) of the castable samples with 4 to 10% MgO amounts indicate quite stable state under different shear rates. Beginning from 10% MgO contents, rheological properties show some degradation.

(2) Variation of the rheological characteristics of the castable samples with time show a critical point, i.e. rheological characteristics of the castable with ≤ 8% MgO show shear thinning, (i.e. torque decrease with time). However, that of the castable with ≥ 10% MgO show shear thinning within 30 minutes, then, shear thickening (i.e. torque increase with time) between 40 and 70 minutes (see Table 6.2.1).

Table 6.2.1 Variation of torque values with testing time under different shear speed (data from Fig. 6.2.9)

τ / speed	Start	10 Min.	20 Min.	30 Min.	40 Min.	50 Min.	60 Min.	70 Min.
0.23	1.397	0.98	0.932	0.919	0.934	0.994	1.16	1.535
0.61	2.146	1.984	1.94	1.94	1.952	2.009	2.128	2.384
0.91	2.48	2.467	2.488	2.483	2.555	2.616	2.712	2.864
0.89	2.421	2.379	2.427	2.44	2.477	2.54	2.587	2.597
0.69	2.032	1.956	1.98	2.01	2.011	2.042	2.112	2.168
0.47	1.623	1.558	1.497	1.527	1.534	1.546	1.627	1.711
0.28	1.113	1.025	1.015	1.05	1.016	1.047	1.082	1.355

(3) With increase in MgO content, torque viscosity and flow resistance values rise; the thick fluid castables is stable within 10 minutes, after which there is no further change with testing time until 60 minutes. The substantial stability of the castables in time before viscosity increase is beneficial for installation.

(4) Rheological behavior of the specimens tested follows a Bingham flow pattern.

6.2.5 Conclusions

From the above experimental results, it may be concluded that MgO addition lower than 10% has very little effect on rheological properties, and 12 wt% MgO addition can be acceptable. Considering overall properties (installation characteristics, strength properties and slag corrosion resistance) at the same time, an optimum addition 8 ~10 wt% MgO is recommended.

The effects of microsilica, ultra fine alumina and MgO addition on rheological behavior of zero cement alumina-based MgO containing castables may be summarized as follows:

1. With increase in content of microsilica addition (from 1% to 5%), rheological properties show shear thinning characteristics, and their yield stress, variation of torque viscosity and flow resistance with testing time are decreased.
2. There is only little change in rheological behavior with variation of ultra fine alumina addition.
3. MgO addition of lower than 10% in castables has little effect on rheological properties, showing shear thinning.

4. The rheological behavior of all samples tested follows a Bingham flow pattern.

6.2.6 References for chapter 6.2

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6.3 RHEOLOGY STUDY ON ALUMINA-MGO-GRAPHITE CASTABLES

This chapter is to be submitted for publication in REFRACTORIES APPLICATIONS AND NEWS, USA, in June 15, 2004.

6.3.1 Abstract

Based on successful manufacture of alumina-magnesia castables and modified extruded graphite pellets, the developments of alumina-magnesia-carbon castables have displayed good prospects in applications for steel ladle. In this work, the rheological behavior of zero cement alumina-based MgO-containing castables with addition of various amount of flake graphite and extruded graphite pellets have been investigated using an IBB rheometer. Their rheological results are compared with corresponding castable samples without carbon addition. It is found that the alumina-based castable with 8% MgO and 4 ~ 6 wt% extruded graphite pellets display a rheological behaviour characteristics of Bingham fluids. They also show good flowability with low water demand (<6.7%) and no segregation during the shearing of castable is observed.

6.3.2 Introduction

In consumption of the refractories in iron and steel making industry, the refractories for ladles have occupied biggest ratio of the refractories item in the total steel production costs. Since the bottom and sidewalls of ladles have been widely formed by using alumina-MgO/spinel vibrated castables in the last decade, the improvement of service life of ladle has been quite fruitful. But with the progress of metallurgical technologies, especially the application of secondary refining process in ladles results in decrease in the service life of these castables. So far, ladle lining is still not entirely lined with castables due to degradation of the ladle slag zone. Hence MgO-C or Al_2O_3-MgO-C bricks are used in the ladle slag zone for maintaining similar service life for ladle sidewalls and slag zone.

From the 1970's, the oxide carbon-containing bricks (MgO-C, Al_2O_3-C and Al_2O_3-MgO-C) have been successfully developed and applied for the steel industry and the advantages of carbon as a main component in refractories have been confirmed. For example, they have superior corrosion resistance because they are not wet by molten metal and slags, they have good thermal shock resistance due to high thermal conductivity etc. Nevertheless, some characteristics of the graphite are weaknesses for use in castables, which impedes development of carbon-containing castables.

Except the merits of carbon, MgO-C or Al_2O_3-MgO-C bricks normally contain higher carbon (>10%) which can be harmful for producing high quality steel (such as ultra low carbon steel or cleaning type steel) because it is possible that the carbon in bricks dissolves into molten steel to degrade steel quality. However, using castables as the bottom and sidewalls of ladles and carbon-containing bricks as slag line materials, two different installation methods lead to difficulties in installation, and drying of lining is also a problem.

Considering three issues in the basic design concept for ladle lining, i.e. entire casting monolithic lining, long service life and low or no impact on molten steel, many studies focus on developing new castables in order to meet the new requirements. In this case, the developments of alumina-based and magnesia-based castables with carbon treated by different methods have exhibited good prospect for application in ladle linings [1~4]. H. Teranishi et al. [1] investigated the effects of various forms of carbon on flowability of castable. The result showed that different carbon forms with same content in MgO-C castables lead to great differences in water content, such as 18 % water for flake graphite containing castable, 9 % water for amorphous graphite and 6 % water for pitch and carbon black. The later is close to that of a conventional Al_2O_3-MgO castable. They found that the MgO castable with 5 wt% addition of pitch and carbon black applied in the slag line of a ladle furnace, lifetime was more than twice that using an Al_2O_3-MgO castable. S. Zhang et al. [2] reported that aqueous wettability and dispersion properties of graphite could be improved using a coating technique with materials such as carbides (SiC) and oxides (Al_2O_3, TiO_2, SiO_2, MgO ZrO_2). The MgO-C castable containing 4 % graphite coated by SiC has 174mm of vibrated flow value with 6.5 % water amount. Whereas for similar vibrated flow value (170mm), the water demand for untreated graphite castable is 11%. M. Rigaud et al. [3,4] developed extruded graphite pellets for use in castables that appear to decrease water amount (below 6.0%) and show good dispersion property and flowability.

To understand and control installation properties of graphite-containing castables, in this work, the rheological behavior of zero cement alumina-based MgO-containing castables with addition of various contents of flake graphite and extruded graphite pellets has been investigated using an IBB rheometer. The rheological results are compared with corresponding castable samples without any carbon addition. This work would be helpful for further development and application of high performance graphite-containing castables by pumping or shooting placement.

6.3.3 Experiments

1) Raw materials

The raw materials used for the rheological tests include fused alumina as aggregates and fillers, fused magnesia, two sorts of graphite additions (flake graphite and extruded graphite pellet), microsilica (Elkem 971U), ultra fine alumina and calcium aluminate cement (Secar 71). Their main chemical compositions and particle size are shown in Table 6.3.1.

The extruded graphite (EG) pellets used are prepared by CIREP, using mixes of natural flake graphite ($C \geq 97.0\%$, <0.074mm), refractory oxide and anti-oxidants with suitable organic binder by extruded method. After heat treatment for curing, the binder is pyrolized to form carbon-bonding in the pellets. Then, surface of the pellets is modified with an organic agent to improve its hydrophilic properties. Lastly, particle size of the pellets is adjusted by crushing and sieving for use. The EG pellets contain 48% ~ 97% fixed carbon depending on the total amount of oxide fillers and anti-oxidants used in the pellets (5).

Table 6.3.1 Compositions and particle size of raw materials

Raw Materials	Composition and Particle Size
Fused alumina	$Al_2O_3 \geq 98.5\%$, 5 ~ 0.088mm, < 0.074mm, D50 = 42.05μm < 0.044mm, D50 = 22.91μm
Fused MgO	MgO≥ 98.5.0%, < 0.074mm, D50 = 40.25μm < 0.044mm, D50 = 20.00μm
Flake graphite	C ≥ 96.0%, < 0.088mm
Extruded graphite pellets	C ≥ 85.0%, 1~4mm, Φ = 1mm
CA cement (Secar 71)	Al_2O_3 69.0~72.2 % CaO 27.0~30.0%, D50 =12.0μm
Microsilica (Elkem 971U)	$SiO_2 \geq 97.0\%$, < 1.2μm, D50=0.51μm
Ultra-fine alumina	$Al_2O_3 \geq 98.5$ %, < 4.0μm, D50 =1.8μm

2) Specimen mix preparation

Similar to previous tests of rheological properties, the ratio of the two particle sizes (< 0.074mm and < 0.044mm) of fused alumina as fillers is 1:1. The ratio of coarse grains and matrix portion is 62:38. An approximate q value of 0.29 is used for design of particle size distribution of the castable samples according to Andreasen's particle size distribution model.

Two groups of alumina-MgO-carbon castable samples with fixed content of 8% MgO powder, 6% ultra-fine alumina and 3% microsilica have been prepared:

(1) The first group of samples with various contents (2, 4 and 5%) of flake graphite; (2) The second group of sample with different content (2, 4 and 6%) of extruded graphite pellets, to compare their effects on rheological behavior of alumina-magnesia castables.

For each rheological test, a 10kg castable mix made from the above composition is uniformly mixed and then well blended with water and wetting agent. The time for wet mixing is controlled at 4 minutes and each cycle testing duration of the rheological measurement is automatically fixed by computer control for 80 seconds.

3) Experimental method

After the alumina-magnesia-graphite castable sample was wet-mixed, vibrated self-flowing value was measured. Then, the IBB rheometer (6) was used for rheological measurements. The experimental procedure was that wet castable mix was poured into a bowl of the IBB rheometer and torque under varying speed is given at 5 minute intervals for 45 minute test durations for each sample. From this, rheological curves (torque vs impeller speed, variation of torque viscosity and flow resistance with time) are obtained to evaluate rheological behavior of the alumina-MgO-graphite castables.

6.3.4 RESULTS AND DISCUSSIONS

6.3.4.1 Effects of flake graphite on rheological behavior

There have been numerous papers reporting the superior properties of alumina-based magnesia containing castables. In alumina-based MgO-containing castables without carbon, microsilica additions react with MgO and water to form magnesia-silica-hydrate bonding system at room temperature as well as with alumina to form mullite at high temperatures. After graphite is added in the castables, the mode of bonding of the castables is not changed. But graphite addition may adversely affect this bonding. To compare rheological behavior of the alumina-MgO castables with different contents and types of graphite, a similar level of vibrated flow-value is controlled by changing the amount of water addition (from 5.3 % to 10.0% for flake graphite containing samples and 5.3% to 6.6% for extruded graphite pellet containing samples). The rheological results of the castable samples are shown in Fig. 6.3.1 to 6.3.6, among them, Fig. 6.3.2 as reference shows the results of samples without graphite.

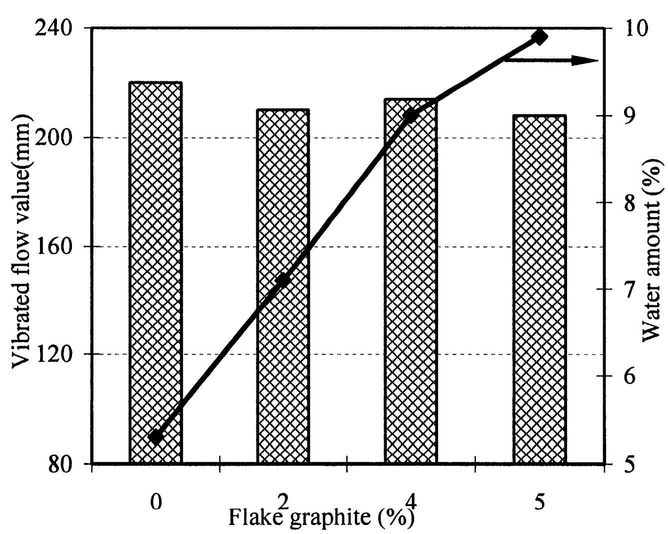

Fig. 6.3.1 Vibrated flow-value vs water amount of the samples with various flake graphite contents

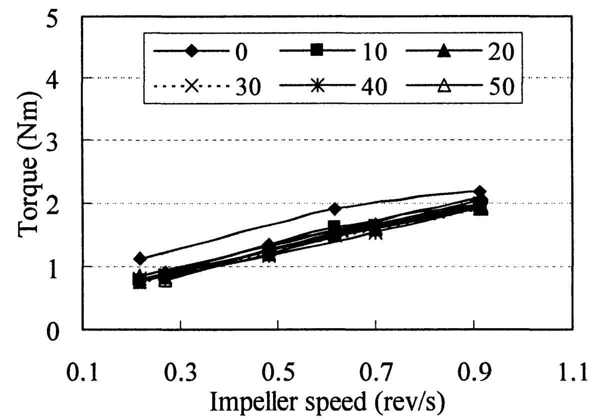

Fig. 6.3.2 Rheological curves of castables without any graphite (5.3 % water)

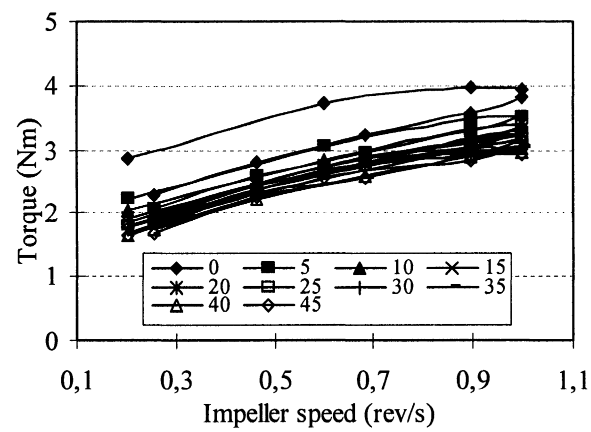

Fig. 6.3.3 Rheological curves of castables with **2 %** flake graphite (6.5 % water)

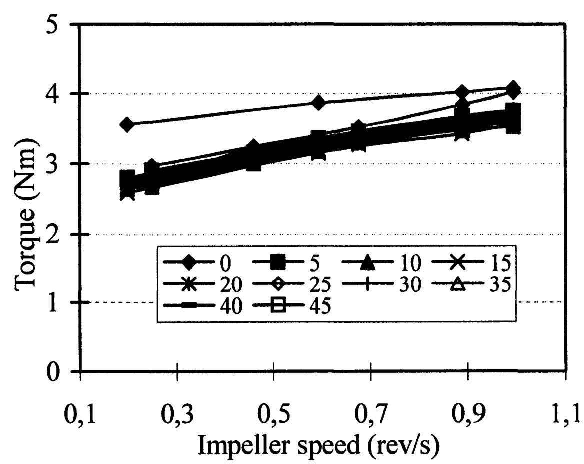

Fig. 6.3.4 Rheological curves of castables with **4 %** flake graphite (8.5 % water)

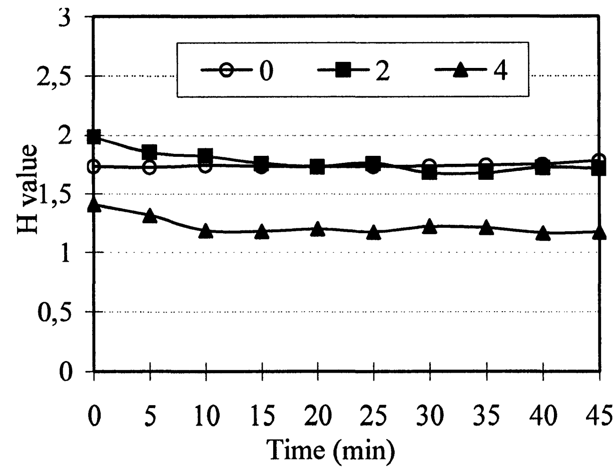

Fig. 6.3.5 Torque viscosity (H) vs testing time of the samples with different flake graphite contents

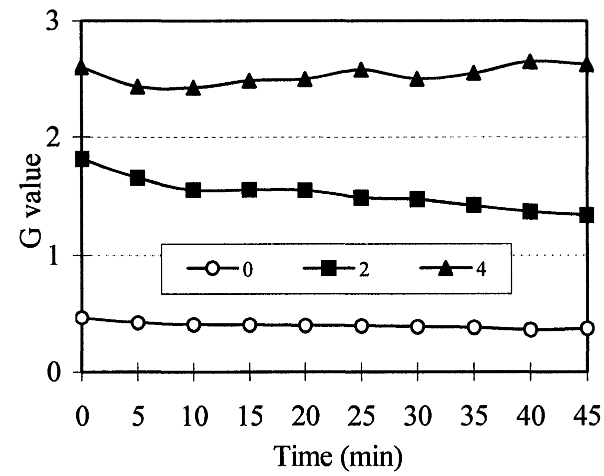

Fig. 6.3.6 Flow resistance (G) vs testing time of the samples with different flake graphite contents

It can be seen from the above rheological diagrams:

(1) With an increase in content of flake graphite, the flowability of the castables tends to be deteriorated due to negative effect of flake graphite addition even when very high water amount is used.

(2) The rheological behavior of the alumina- based MgO containing castables without flake graphite is much better than that of castables with flake graphite, showing low torque, flow resistance and the lowest water demand in shearing.

(3) With increase in flake graphite contents (from 2% to 5%) and corresponding increase in water content (from 5.3% to 10%), torque and yield stress at varying shear rates are increased, i.e. the rheological properties are deteriorated.

(4) The structure of the castables tends to be homogenized after the first shearing cycle. The change of shear torque is very little within 45 minutes. All specimens display Bingham fluid characteristics.

(5) During 40 minute testing time, torque viscosity (H) and flow resistance (G) values of the castable sample exhibit slight change with testing time. Whereas the castable sample with higher content of flake graphite shows lower H values due to lubrication of the graphite and higher G values due to non-homogenization of the flake graphite containing castables.

The deterioration in rheological properties of flake graphite containing castables is due to the two main drawbacks of graphite:

- Poor wettability by water, leading to difficulties in dispersion and flowability of the castables, thus high water demand has to be needed.
- The large difference in specific gravity between flake graphite and refractory oxide, resulting in segregation, (mainly floating of graphite).

Therefore, flake graphite has noticeably negative effects on rheological properties of castables.

6.3.4.2 Effects of extruded graphite pellets on rheological behavior

The rheological measurements are carried out under the following testing conditions: suitable flow values of the castable samples are controlled for smooth shearing by varying amount of water addition (from 5.3 % to 6.6%). The rheological results of the castable samples with different contents of extruded graphite pellets (2, 4 and 6%) are shown in Fig. 6.3.7 to 6.3.12.

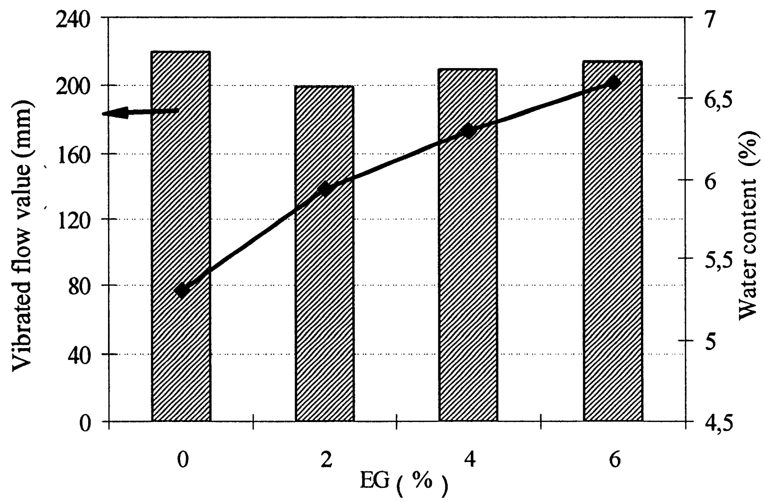

Fig 6.3.7 The vibrated flow value vs water amount of the samples with varying EG graphite contents

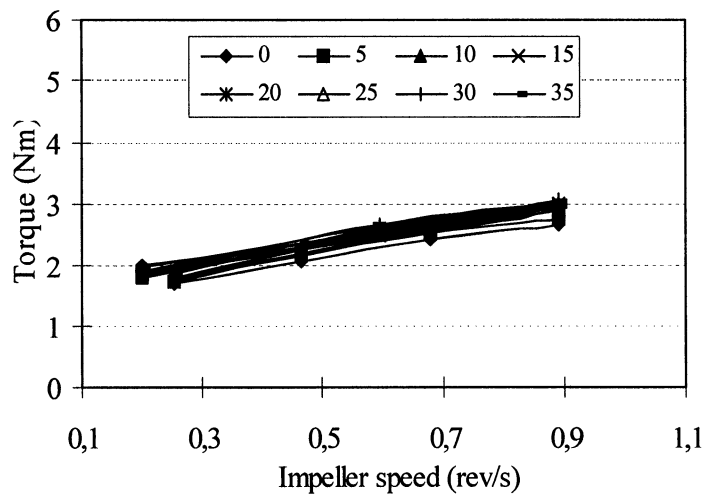

Fig 6.3.8 Rheological curves of the castables with 2% EG graphite

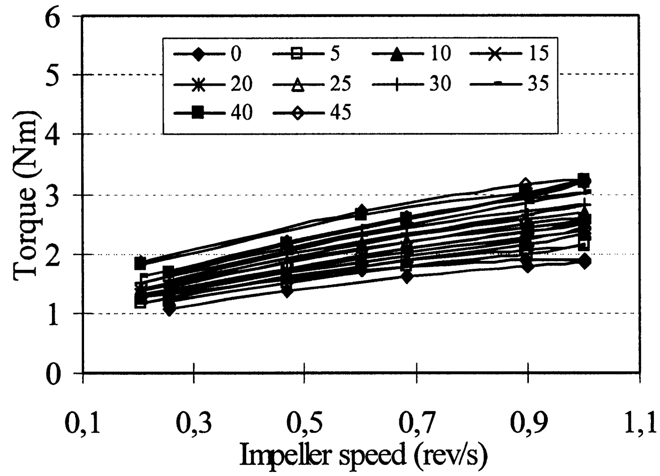

Fig 6.3.9 Rheological curves of the castables with 4% EG graphite

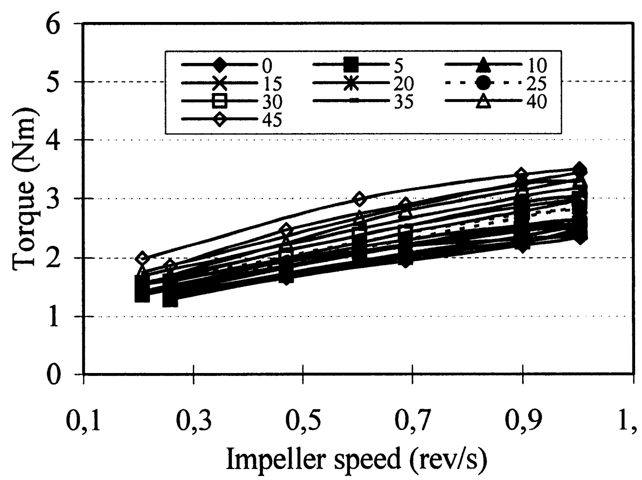

Fig 6.3.10 Rheological curves of the castables with 6% EG graphite

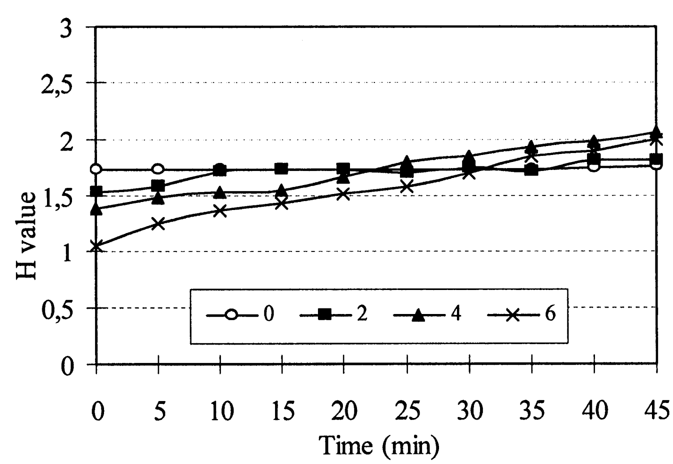

Fig 6.3.11 Torque viscosity (H) vs time of the samples with different EG graphite contents

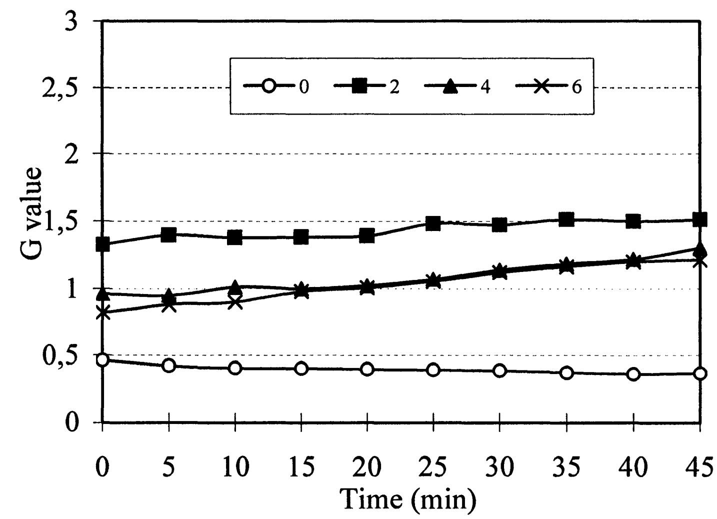

Fig. 6.3.12 Flow resistance (G) vs time of the samples with different EG graphite contents

It is found from Fig. 6.3.7~ 6.3.12 that:

(1) Comparing with castable without any graphite, rheological properties (torque, yield stress values) of the castable samples with EG pellets under different shear rates show degradation. However, the degree of the degradation is much less than that of the castable with flake graphite addition; the torque and yield stress values are lower even when water addition is reduced by 33% (from 10% to 6.6%).

(2) With increase in content of EG pellets, torque and flow resistance values are slightly increased, and water demand is increased. The rheological behavior of the castables with 4% and 6% EG graphite is very similar and there is only little change in water demand (from 6.3% to 6.6%).

(3) There is a substantial stability in torque viscosity and flow resistance of the castables

with elapse of testing time within 45 minutes. The rheological behavior of the specimens tested follows a Bingham flow pattern.

Typical rheological parameters of the castables with two types of graphite additions are listed in Table 6.3.2 for comparison.

Table 6.3.2 The comparison of rheological parameters of castables with different graphite addition

Rheological Parameter	Flake Graphite, (4%)	EG Pellets (4%)	No Graphite
Water addition, wt%	**9**	**6.3**	**5.3**
Flow value, mm	214	212	220
Torque*, Nm			
10 minutes	3.60/3.179	2.44/2.064	1.98/1.598
40 minutes	3.75/3.362	3.24/2.668	1.98/1.484
H value, Nm.s			
10 minutes	1.188	1.536	1.736
40 minutes	1.166	1.977	1.907
G value, Nm			
10 minutes	2.422	1.009	0.404
40 minutes	2.648	1.216	1.497

* Under impeller speed (= 0.6 &0.9 rev/s)

According to the rheological testing results and flowability of the castables, to evaluate workability of the castable for pumping, it may be concluded that the alumina based MgO containing castables with EG pellets have much better rheological properties than with flake graphite and also ensures adequate working time. Therefore, assessing from rheological properties and water demand, the alumina-based castable with 8% MgO and 4 ~ 6% EG pellets is suitable for pumping installation.

In graphite containing castables, the significant improvement of rheological properties of the EG pellets containing castables is because the graphite pellets prepared by extruded method and surface treatment possess much improved characteristic in hydrophilic and dispersion properties as well as specific gravity and porosity. Therefore, the EG pellets containing Al_2O_3-MgO castables may have good prospect for applications in ladle lining as pumpable and shotcreting castables.

6.3.5 Conclusions

The rheological behavior of MgO containing alumina-based castables with flake graphite and extruded graphite pellets is summarized as follows:

1. Two types of the graphite additions have negative effects with different degrees on rheological properties of the castables. But the rheological behavior of extruded graphite pellets containing castables is much better than that of flake graphite containing castables under test condition of much lower water demand (water content reduced by water 30 wt%) at varying shear rates.
2. With increase of flake graphite and EG pellet additions and corresponding increase in water content, rheological properties (torque and flow resistance at varying shear rates) of

the castables are degraded, the former is much severe in degree.

3. The better rheological properties of the EG pellets containing castables is because of improvement in hydrophilic and dispersion properties of EG pellets prepared by extrusion method and surface treatment. The alumina-based castable with 8% MgO and 4 ~ 6% EG pellets is suitable for pumping installation, assessing from rheological properties.
4. There is little change in rheological behavior with testing time. The rheological behavior of the castable samples tested follow Bingham flow pattern.

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CHAPTER 7 SUMMARY, MAJOR CONCLUSIONS AND RECOMMENDATIONS

With self-flow and pumping refractory castables finding more and more applications, rheology of such castables becomes a new concern and a growing field of investigation. In a cooperative program between Ecole Polytechnique, Canada and Zhengzhou University, China initiated in 2000, it was decided to tackle such a subject starting with the rheological behavior of bauxite- and alumina-based castables. By this study, the parameters which influence the shear thinning or shear thickening, as measured by torque viscosity and yield stress values, have been determined for self-flow and pumpable castables. The goals of this work were to identify the rheological parameters and how to control them, and to understand the rheological properties of bauxite- and alumina-based refractory castables and how they are influenced.

Based on the results of the studies, it is now well-established how to design castable system with good rheological properties for pumping:

- bauxite-based SiC containing castables, for iron making industry;
- alumina-based castables with magnesia and /or extruded graphite pellets for steel making industry.

The results and the published papers about those rheological investigations are new in the refractory research field, especially, for alumina-MgO, alumina-carbon and alumina-MgO-carbon castables. For those three systems, no similar work has been previously presented. Furthermore, based on the research work, the industrial trials on the suggested SiC-containing bauxite-based shotcrete have been successfully carried out in torpedo car (capacity 260T) at Capital City Iron and Steel Company of Beijing [66] in 2003.

Optimization of rheological behavior of the castables investigated has been realized in the following ways:

1) Controlling the total content and ratio of microsilica and ultra fine alumina;
2) Controlling the right PSD;
3) Selecting suitable dispersants for a good flowability;
4) Optimizing cement content and water/cement ratio;
5) Optimizing content of fillers (SiC, MgO and/or EG pellets additions);

In total, more than 200 different mixes and samples have been prepared, and their rheological behavior was studied. For this purpose, three methods have been used:

- Rotational viscometer —for studying rheology of matrix slurry;
- Flow table — for measuring self-flow ability of castables;
- IBB Rheometer —for studying rheology of castable mixes.

To further characterize the samples, high temperature properties, conventional three point bending method has been adopted for measurements of HMOR, MOR- temperatures and stress-strain relationships. Residual strength ratio after thermal shock cycling from 1200 ^{o}C to water-cooling and relationship of critical temperature difference (ΔT) vs. residual strength have been used for evaluating their thermal shock resistance.

A. Major results and conclusions

The major results and conclusions are summarized as follows:

I. Study on the rheological behaviour of matrixes of bauxite-based castables

The components in the matrix investigated, such as super-fine silica and alumina addition, water/cement ratio, dispersants and bauxite particle-size, have effects with different degree on viscosity, shear rate and shear stress of the slurries. It is proven that among them ultra fine powder (microsilica and ultra fine alumina) and dispersants are the main controlling factors. Among the dispersants investigated, Polycarboxylateether (Castament FS-20) is the most effective in reducing viscosity, shear stress and yield stress of the slurries. Its optimum addition amount is 0.20 wt %.

Viscosity of matrix slurry is noticeably reduced with an increase of microsilica amount, but it is slightly increased with ultra fine alumina amount. With a decrease in the water/cement ratio, viscosity and shear stress are slightly increased up to water/cement ratio close to 2 (19/9). The rheological behavior of slurries exhibits the characteristics of a Bingham fluid.

Based on these results, the range of optimum composition of the matrix with good rheological behavior has been obtained for the rheology study of the castables.

II. Study on the rheological behavior of bauxite-based SiC-containing castables

Rheological behavior of the bauxite-based SiC containing castables with low or ultra-low cement content and microsilica as bonding system exhibits shear-thinning characteristics and follows Bingham flow pattern. With variation of silicon carbide content from 0 to 16%, the rheological properties (torque, yield stress, variation of torque viscosity with testing time and flow resistance) of the castables are degraded; optimum SiC content in the castables is 4 % to 8%.

In the bauxite-SiC castables with ultra low-cement content, the effect of cement on rheological behavior is very weak. But in the low-cement bauxite-SiC castables, the cement content has a significant negative influence on the rheological behavior.

III. Study on the high temperature mechanical properties of bauxite-based SiC-containing castables

1) HMOR and relationship between MOR vs temperatures

SiC addition in ULC bauxite-based castable specimens has remarkable effect in improving HMOR at 1400 °C. For specimens containing ultra fine Al_2O_3 / SiO_2 =75/25, HMOR increases with increase of SiC contents, whereas for specimens containing ultra fine Al_2O_3 / SiO_2 =25/75, the optimum SiC addition is 4 ~ 8%. MOR–T curves illustrate that MOR increases at first with temperature up to 800 °C or 1000 °C, after which MOR decreases significantly.

2) Stress-strain relationship

The stress-strain behavior of the specimens may be divided into three stages: elastic range from RT to 600°C; "plastic flow range" (600°C~1000 °C) and " viscous flow" range (1000°C and above).

3) TSR behavior

SiC addition is also very effective in improving TSR of castable specimens. With increase of SiC contents, significant increase in residual strength ratio is observed, with maximum values at 4 ~ 8% SiC addition.

The positive effects of SiC addition on HMOR and TSR of bauxite-based castables may be explained since: (a) SiC possesses lower thermal expansion, higher thermal conductivity and higher strength; (b) SiC crystals are mostly prismatic or elongated and are more resistant to thermal stresses; (c) SiC crystals interlaced into corundum-mullite structure create a reinforcing effect.

IV. Study on the rheological behavior of ultra-low cement alumina based castables with and without graphite

When ultra fine alumina and microsilica additions are used together in such castables, an increase in microsilica content would lead to significant improvement of rheological properties of the castables. Microsilica is thought to be the controlling factor affecting the rheological properties and helps to achieve good flowability and to assure adequate working times. When ultra fine alumina/microsilica ratio is higher than 50:50, rheological properties tend to degrade, showing higher torque and yield stress values. In order to obtain satisfactory high- temperature properties, ultra fine alumina/ microsilica ratio has been recommended to be in between a 50/50 to 25/75 ratios.

PSD strongly affects rheological behavior of castables. For castables with a fixed lower q value, its rheological behavior can be considerably improved by adjusting microsilica content.

With an increase of either flake graphite or EG pellet additions and even with a corresponding increase in water content, rheological properties (torque and flow resistance at varying shear rates) of the castables are degraded. Both flake graphite and extruded graphite pellets additions have negative effects of different degrees on rheological properties of the castables. But the rheological behavior of extruded graphite pellets containing castables is much better than that of flake graphite containing castables, even at much lower water demand (water content reduced by water 34.4 wt%) at varying shear rates. In terms of rheological properties, the order of merit of carbon additions is: no graphite > EG pellets >> flake graphite. The rheological behavior of the all mixes tested follow Bingham flow pattern.

The better rheological properties of the EG pellets containing castables is due to improvements of properties of hydrophilic and dispersion graphite mixes by extrusion method and surface treatment of EG pellets.

V. Study on zero cement alumina-based MgO-containing castables with and without graphite

With increase in content of microsilica addition in MgO containing castables without any graphite, rheological properties show shear thinning characteristics. Torque and yield stress, variation of torque viscosity and flow resistance with testing time are remarkably decreased.

MgO addition of lower than 10% in castables has little effects on rheological properties, showing shear thinning characteristics. Optimum range of MgO content is 6% to 10%.

The graphite additions, either flake or extruded pellets, have negative effects with different degrees on rheological properties of the castables. The rheological behavior of extruded graphite pellets containing castables is much better than that of flake graphite containing castables under test condition of much lower water demand (water content reduced by water 30 wt %) at varying shear rates. This can be explained by the inherent advantages of

EG pellets over flake graphite, in terms of hydrophilic and dispersion properties.

The rheological behavior of the castable mixes tested shows Bingham fluid characteristics. Based upon the measured rheological properties, the alumina-based castable with 8% MgO and 4~6% EG pellets should be suitable for pumping installation.

B. Recommendations

Based on the above conclusions, the following recommendations are given for the good formulations of the castables with good rheological behavior and for further developing work:

Considering rheological behavior as well as high temperature properties, for bauxite- and alumina-based castables without magnesia addition, optimum range of the ultra fine alumina and microsilica ratio (Al_2O_3/SiO_2) should be controlled between 50/50 to 25/75. In bauxite-based SiC-containing castables, 4% ~8 % SiC and 2% ~ 4% calcium aluminate cement are moderate amounts. Choosing PSD with q =0.23, and the ultra fine alumina and microsilica ratio = 25/75, optimum rheological properties can be obtained.

For MgO containing alumina-based castables, suitable content of MgO addition is between 6% to 10%; and 3% microsilica is required for good rheological behavior, appropriate flowability and working time, at same time to limit the volume expansion due to formation of mullite at high temperature.

To develop graphite containing alumina-based castables, extruded graphite pellets are an appropriate carbon source, up to 4% to 6% amounts, with good rheological behavior tested under low water amount (<6.3%).

Until today, including previous work [62~65] and the thesis work, systematic investigations on EG pellet containing castables have been done in CIREP. The fundamental work has been established. It is proven that the castables have wide prospect in applications for iron and steel making industry. Based on these presented studies, an important issue, in future work, will be to test the products in practical applications and to accelerate the commercialization of the EG pellets. In this context one may think about making use of China's wide iron and steel industry`s market to extend the subject. At the same time, this may be also an extending field of cooperation between CIREP and HTCI.

According to the characteristics in properties of the castables with EG pellets, two main aims for application should be considered:

- Developing alumina-carbon functional monolithic refractories (still using isostatic pressing) for continuous casting steel; such as long nozzle, submerged entry nozzles and stopper- monoblock. Now, this type of functional refractories is mostly composed of alumina-carbon monolithic materials with 15~30% carbon contents.
- Developing alumina-MgO-carbon castables for ladle lining, in particular at the slag line zone.

For these purposes, service properties at high temperatures, such as abrasion by molten steel, corrosion by slag and thermal shock resistance have to be emphasised. Simulation tests under service condition are still necessary.

C. Industry trial of bauxite-SiC-C refractory shotcrete

Based on the study on rheology, two industrial trials of wet spraying technique of Al_2O_3-SiC-C castable were carried out in molten iron torpedo car (Capacity: 260T) of Capital

Iron and Steel Company of Beijing. To obtain good pumpable and sprayable properties, effects of particle size composition, ultra fine powder and setting agents on rheological behavior and installing properties were reconfirmed in the practice. The equipment for the wet-spray process was from Krosaki Harima Corporation of Japan (see Fig. 7.1). Spraying speed of the pumping castable was controlled to 4 ~ 4.5 T/h. Total 20T castable was used to repair residual brick lining. Originally, average life of the torpedo car lining was 900 heats (no reparation). By the spraying reparation, its service life was increased to over 1200 heats and the repairing layer has being still used until the statistic. The results of industrial application of the wet spraying Al_2O_3-SiC-C castable show that the pumping and spraying installation of the castable with low rebound (< 5%) was successful and service life of the lining was prolonged by over 35%.

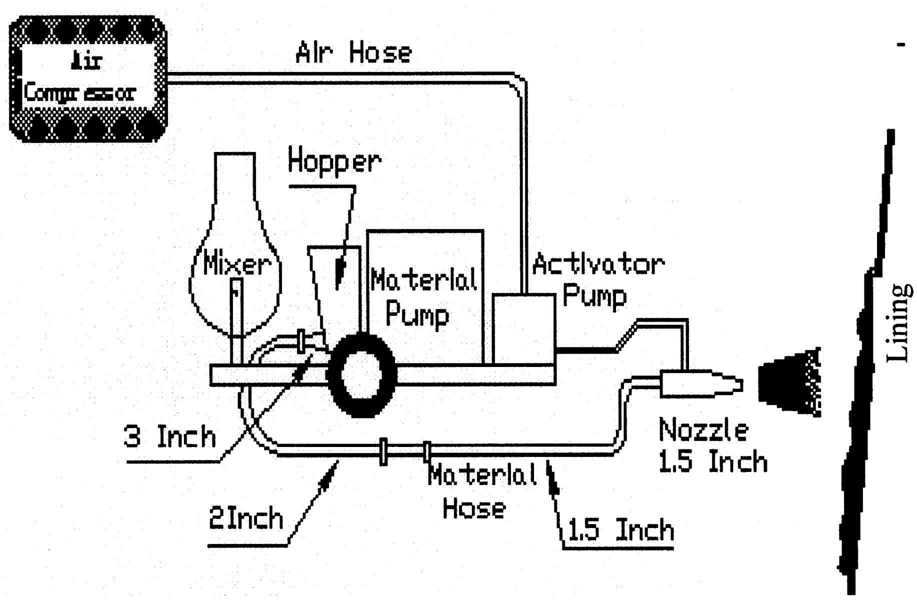

Fig. 7.1 Schematic set up of wet spraying

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