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The Sonochemical Extraction of Monazite Using Sulfuric Acid

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Département de génie chimique

Mémoire présenté en vue de l'obtention du diplôme de *Maîtrise ès sciences appliquées*

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POLYTECHNIQUE MONTRÉAL

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:

The Sonochemical Extraction of Monazite Using Sulfuric Acid

présenté par **Sachinthana SAMARAKONE**

en vue de l'obtention du diplôme de *Maîtrise ès sciences appliquées*

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RÉSUMÉ

La technique de lixiviation assistée par ultrasons a été utilisée pour extraire les lanthanides (cérium, néodyme, samarium) de la monazite en utilisant de l'acide sulfurique. Les paramètres technologiques tels que le temps de réaction, la concentration en acide, la densité de la pulpe et la température ont été évalués. Les conditions optimales de lixiviation sont les suivantes : H_2SO_4 à 98 %, puissance ultrasonique de 102 W, rapport liquide-solide de 7:1, température de la matrice à 60 °C et temps de réaction de 30 minutes. Par rapport à la lixiviation silencieuse, les ultrasons ont amélioré les récupérations d'au moins 1,5 fois pour tous les lanthanides étudiés pendant la durée de l'étude. Dans des conditions optimales, la récupération a atteint 31,9 %, 30,7 % et 32,8 % pour le cérium, le néodyme et le lanthane respectivement. Comparativement, les méthodes de lixiviation silencieuses n'ont donné que 21,8 %, 20,8 % et 22,7 %. Les tests ultrasonores ont en outre amélioré les récupérations à 41 % pour les trois terres rares après deux étapes de lixiviation dans des conditions optimales. Les raisons de l'amélioration par ultrasons étaient dues à la cavitation, qui entraînait une augmentation des collisions avec les particules, ainsi qu'à des microjets qui attaquaient la surface des particules, facilitant la rupture des cristaux. En outre, des expériences supplémentaires ont été menées pour comparer des acides inorganiques courants tels que HCl , HNO_3 et H_2SO_4 . Des récupérations de terres rares plus élevées ont été obtenues avec HCl et H_2SO_4 , tandis que les résultats avec HNO_3 ont été jugés peu fiables en raison de l'érosion de l'alliage monel (cuivre-nickel) utilisé dans le sonotrode. Malgré des améliorations claires dans la récupération des terres rares par rapport aux conditions de lixiviation silencieuse dans cette étude, l'enquête a utilisé jusqu'à huit fois l' H_2SO_4 utilisé lors des méthodes d'extraction conventionnelles dans l'industrie, et a encore donné des valeurs d'extraction inférieures, par rapport à la récupération de 95 % des terres rares lors des méthodes conventionnelles à haute température dans l'industrie. Toutefois, les tendances de récupération des terres rares au cours de l'étude ont démontré une amélioration claire de l'extraction des terres rares par rapport aux conditions silencieuses et le fait que ces résultats aient été obtenus en seulement 30 minutes et à 60°C indique que l'expansion de la recherche pour analyser la sonication à des températures modérées de 80-90°C et l'optimisation de la conception du réacteur pourrait conduire à des économies d'énergie, de coûts et de temps de réaction par rapport aux méthodes industrielles.

ABSTRACT

The ultrasonic-assisted leaching technique was used to extract lanthanides (cerium, neodymium, samarium) from monazite using sulfuric acid. Technological parameters such as reaction time, acid concentration, pulp density, and temperature were evaluated. The optimum leaching conditions were as follows: 98% H_2SO_4 , 102W ultrasound power, 7:1 liquid-to-solid ratio, 60°C matrix temperature and 30 minutes reaction time. In comparison to silent leaching, ultrasound improved recoveries by at least 1.5-fold for all lanthanides investigated for the duration of the study. Under optimal conditions, the recovery reached 31.9%, 30.7% and 32.8% for cerium, neodymium and lanthanum respectively. Comparatively, the silent leaching methods only yielded 21.8%, 20.8% and 22.7%. The ultrasonic testing further improved recoveries to 41% for all three REEs upon two stages of leaching in optimal conditions. The reasons for the improvement by ultrasound were due to cavitation resulting in increased collisions with particles in addition to microjets that attacked the particle surface, facilitating the crystal breakdown. Furthermore, extra experiments were conducted to compare common inorganic acids such as HCl, HNO_3 and H_2SO_4 . Higher REE recoveries were achieved with HCl and H_2SO_4 , while the HNO_3 results were deemed unreliable due to erosion of the monel (copper-nickel) alloy used in the sonotrode. Despite clear improvements in REE recovery compared to silent leaching conditions in this study, the investigation used up to eight times the H_2SO_4 used during conventional extraction methods in industry, and still yielded lower extraction values, compared to the 95% REE recovery during conventional high temperature methods in industry. However, the REE recovery trends during the investigation demonstrated a clear improvement in REE extraction over silent conditions and the fact that these were achieved in just 30 minutes and 60°C indicated that expanding the research to analyse sonication under moderate temperatures of 80-90°C and optimizing reactor design could lead to savings in energy, costs, and reaction times when compared with industrial methods.

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LIST OF ABBREVIATIONS

D2EHPA - Di-(2-ethylhexyl)phosphoric acid

DOA - di-n-octylamine

EDTA - Ethylenediaminetetraacetic acid

EHEHPA - 2-ethylhexyl phosphoric acid-2-ethylhexyl ester

HEHEHP - 2-Ethylhexylphosphonic acid mono-2-ethylhexyl ester

HREE - Heavy Rare Earth Elements

LREE - Light Rare Earth Elements

LS - Liquid Solid

NMC - Lithium-Nickel-Manganese-Cobalt-Oxide

PCB - Printed circuit board

PFD - Process Flow Diagram

PPI - tetra anion diphosphate

PVDF - Poly(vinylidene fluoride) PVDF

REE - Rare Earth Elements

REH - Rare Earth Hydroxides

REO - Rare Earth Oxides

RTP - Room Temperature and Pressure

SEM - Scanning Electron Microscope

SL - Solid Liquid

STP - Standard Temperature and Pressure

SX - Solvent Extraction

TBA - Trybutylamine

TBP - Trybutylphosphate

UEx - Ultrasound Assisted Extraction

XRD - X-ray Diffraction

XRF - X-ray Fluorescence

LIST OF SYMBOLS

σ – Surface tension, kg/s²

t – Time, s

R – Bubble Radius, m

P_0 – Ambient Pressure, N/m²

$R_{\max}$ – Radius of bubble prior to collapse, m

$R_{\min}$ – Minimum radius a bubble can start forming from, m

P_m – Liquid pressure at bubble collapse, N/m²

$P_{\max}$ – Maximum liquid pressure prior to transient bubble collapse, N/m²

$T_{\max}$ – Maximum temperature prior to transient bubble collapse, K

T – Temperature of system or medium, K

ρ_0 – Bulk liquid density, kg/m³

η – shear viscosity, m²/s

P_∞ - Liquid pressure at distance from a bubble, N/m²

P_L - Liquid pressure, N/m²

P_v – Vapour pressure, N/m²

R_0 – Undisturbed bubble radius, m

κ – Polytropic index

P_v – Vapour pressure, N/m²

f – Ultrasound frequency, Hz

ρ – Density, kg/m³

c – Ultrasonic velocity, m/s

η_s – Shear viscosity, m²/s

η_B – Bulk viscosity, m²/s

γ – Ratio of specific heats within gas bubbles

C_P – Specific heat, J/kg

m – mass, g, kg

ΔT – Change in temperature, K

h – heat transfer co-efficient, W/m²K

P_{diss} – Dissipated power during sonication, W

A_{probe} – Area of probe, m²

D_{probe} – Diameter of probe, m

I_{diss} – Dissipated Intensity during sonication, W/m²

A – Amplitude of vibrations, m

k_d – Mass transfer co-efficient

A_p – Total surface area of particles, m²

C_0 – Initial solvent concentration, mol/L

π – Thickness of liquid boundary film, m

D – Diffusivity, m²/s

E – Ultrasonic power dissipated per unit mass of liquid

μ_L – Particle viscosity, mol/m³

ρ_L -particle density kg/m³

V – molar volume, m³

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CHAPTER 1 INTRODUCTION

1.1 Background

Rare earth elements are a group of 15 elements (17 with Yttrium and Scandium which exhibit similar properties and are commonly found in the same ore bodies) with similar physical and chemical properties. These properties include colour, electrical conductivity, solubility and complex formation. Slight variations in properties lead to specific uses for various REEs. The recent push for sustainability has pushed REEs to the forefront of research, largely due to their vitality in green technology products such as wind turbines, magnets in electric vehicles and solar panels. They are also essential in electronics, superconductors, medical and nuclear technological products due to their distinct conductive, spectroscopic and magnetic properties (Balaram, 2019).

Currently, China still dominates the market in terms of REEs with 60% of current production (*Mineral commodity summaries 2022*, 2022). They also have 36% of the world's reserves and have implemented stringent protection policies on their exports (Jha et al., 2016). This had led a supply risk in developed regions such as the United States and Europe and have led to many efforts to mitigate potential shortages. The worldwide demand for REE supplies is steadily increasing and is expected to double in the next decade (Balaram, 2019).

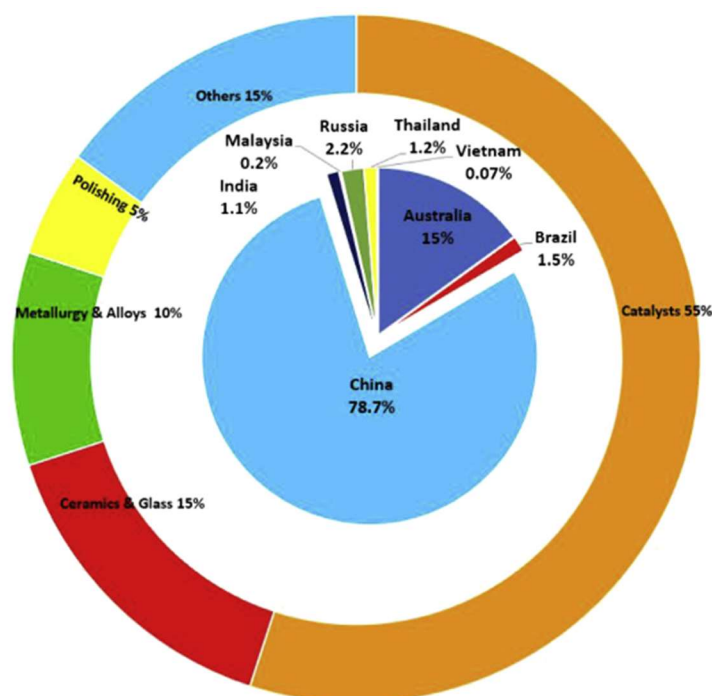


Figure 1.1: Production locations and uses of REEs taken from Balaram (2019)

Most REEs are deposited within the earth's crust in various ores. Around 200 different species of REE bearing minerals are thought to exist, largely in compounds of carbonates, halides, phosphates, oxides and silicates (Kanazawa & Kamitani, 2006). They can be divided into light rare earth elements (LREEs) with the atomic number ranging from 57-63 and heavy rare earth elements (HREEs), which range from 64-71. As mentioned previously, Yttrium and Scandium are additionally included as heavy rare earth elements, in order to provide a total of 17 rare earth elements as they are classified today (Humphries & Library of Congress. Congressional Research Service, 2010). Out of the extensive minerals, there are three that make up about 95% of the world's REE reserves. These are: Bastnasite $[(Ce,La)CO_3F]$, 70-75% REOs], Monazite $[(Ce,La)PO_4]$, 55-60% REO] and xenotime $[YPO_4]$, 55-60% REO]. Another important mineral is known as ion adsorption clays. The former three make up a majority of the commercial sources of REEs. Bastnasite and Monazite account for most of the LREEs while HREEs are extracted primarily from Xenotime and ion adsorption clays (Suli, Ibrahim, Aziz, Deraman, & Ismail, 2017).

Bastnasite is obtained largely from rare earth mines where they exist in the deposits. Conversely, monazite is mined as minerals beach sands and is a by-product of other economically valuable

minerals like ilmenite and rutile processing (Jha et al., 2016). Due to its coexistence with other more economically viable metals present in these heavy minerals sands which are present in many countries, it could become the primary source of rare earths in the world (Berry, Galvin, Agarwal, & Safarzadeh, 2017). Therefore, methods to improve its extraction are constantly being developed.

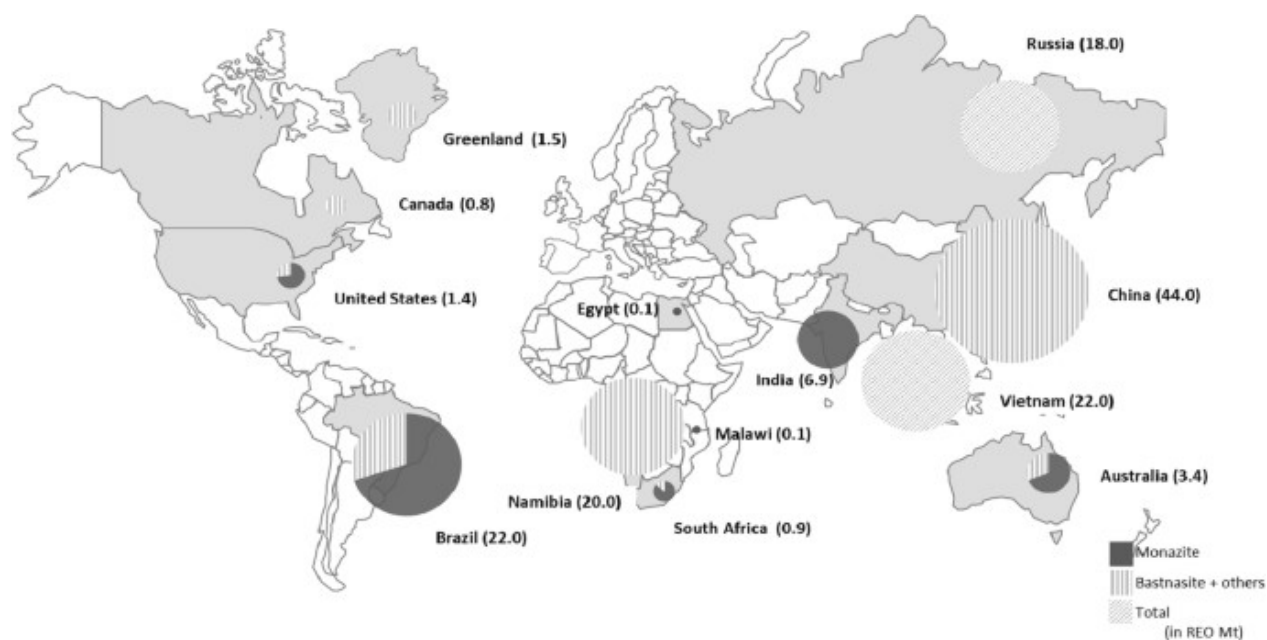
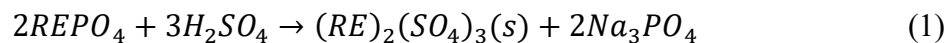


Figure 1.2: Location of various REE source minerals taken from Teixeira, Silva, Avelar, Majuste, and Ciminelli (2019)

Hydrometallurgy is currently one of the most prominent methods of extracting metals from their ores. It is commonly used to extract REEs from their ores. They are usually first concentrated before being leached. Common concentration methods could include gravity separation, magnetic separation and electrostatic separation while some ores can first be concentrated using methods like flotation (F. Habashi, 2013).

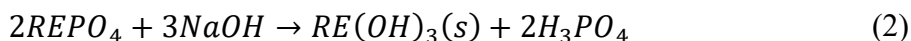
Ore grade monazite is considered difficult to breakdown by simple acid leaching due to its strong crystalline structure (E. Kim & Osseo-Asare, 2012) and therefore require harsher conditions. Sulphuric acid at high temperatures have however been used to react with the REEs, where the sulphate ion (SO_4^{2-}) acts as a ligand which reacts with the REEs. 98% H_2SO_4 at 200-230°C is commonly used to treat the monazite and the reaction is as follows:



After which the solid REE sulfates can be leached with cold water.

It is historically one of the two most common ways to extract REEs. Direct leaching of monazite with different acids has been extensively studied and will be covered in Chapter 2.

A common problem with sulphuric acid leaching method is the loss of useful phosphates and the impurity of the product being formed (Amer, Abdella, Wahab, & El-Sheikh, 2013; Panda et al., 2014). A great way around this issue is the alkaline treatment method, where concentrated NaOH is added to monazite at high temperatures and recovers sodium phosphate as a marketable by-product (C. K. Gupta & Krishnamurthy, 1992). Common reaction conditions are 60-70% NaOH at approximately 150°C for 2-4 hours (Hart & Levins, 1988; Soe, Shwe, & Lwin, 2008). The reaction proceeds as follows:



The resulting REE hydroxides are dissolved using various leaching agents at different conditions.

It is important to note that the sulfuric acid method is still commonly used in large deposits such as the Batou rare earth deposits (Z. Zhang, Jia, & Liao, 2015) and by the Lynas Corporation (Demol, Ho, & Senanayake, 2018). **Therefore, ways to improve this method is important and a method to do this will be investigated in this study. More about the leaching of monazite will be discussed in 2.1.2.**

In order to understand why improving extraction of primary sources remains the greatest concern, we should note that current rates of recycling of rare earths are less than 2% due to inefficient collection, insufficient separation technology and price issues. The prices of these REEs have fluctuated over the years and while there has been a recent boost in these, they are still currently seen as too low to make recycling a viable option in the near future (Patil, Paetzl, Struis, & Ludwig, 2022). This is further exacerbated by the fact that the recycling market is expected to remain small for the coming years as a lot of these products have only been recently introduced and have long lifetimes (Nassar, Du, & Graedel, 2015). Therefore recycling is currently an unfeasible option to meet demand. Patil et al. (2022) states that the EU has conducted criticality

assessments that have taken into consideration the environmental, economic and supply risk-related impact of REEs and thus far described them as “highly critical” (Mueller, Wäger, Turner, Shaw, & Williams, 2017). Since the demand of these materials are increasing every year, these assessments progressively more important. A combination of all these factors makes it reasonable to assume that for the moment, at least, greener methods to extract REEs from primary ores is essential.

The use of alternative energies is one such way to do this with sonication coming to the forefront of research in recent times ("Chapter 4 Ultrasound-assisted leaching," 2007). Extensive literature exists to indicate that ultrasonic vibrations have been shown to increase leaching efficiency. These vibrations can cause pitting and micro-cracks in particles, which in turn lead to an increase in leaching efficiency. Furthermore, the solid-liquid interface is also disturbed during sonication and can facilitate faster movement through the boundary layer ("Chapter 4 Ultrasound-assisted leaching," 2007; Swamy, Katragadda, Narayana, Murty, & Ray, 1995). Ultrasound in leaching will be thoroughly covered in 2.2.2.

1.2 Objectives

Studies indicate that sonication could be applied to improve monazite leaching and the main objective of this research is to deeply review the literature on monazite leaching and extraction and evaluate whether sonication can be used to directly leach monazite using sulfuric acid under mild conditions. A further objective is to obtain engineering data on the process. The clear goal and scope is defined later in Chapter 3.

CHAPTER 2 LITERATURE REVIEW

In order to achieve the objectives mentioned, a thorough literature survey of relevant works regarding both monazite treatment and sonication will be conducted in order to provide the reader with an understanding of the topic. In addition to monazite leaching, the review will provide a brief overview on beneficiation of the monazite before delving into monazite treatment. It then proceeds to ultrasound, covering the theory and using select relevant works to emphasise the concepts in sono-chemical leaching of metals.

2.1 Monazite Treatment

2.1.1 Beneficiation

Monazite is traditionally mined as a by-product of rutile, ilmenite and zircon processing. It also contains the radio-active elements of thorium and uranium which must also be removed (C. K. Gupta & Krishnamurthy, 1992). These heavy sands contain large amounts of light gangue materials which must be removed (Ferron, Bulatovic, & Salter, 1991). The two main methods to do this involve the use of gravity separation, flotation or a combination of both (Chi, Xu, Zhu, Xu, & Qiu, 2001; Jordens, Cheng, & Waters, 2013). Gravity separation is very popular for beach sands and traditionally involves two concentrators in order to reach concentrations of 80-90% heavy minerals (C. K. Gupta & Krishnamurthy, 1992). Once gravity separation has taken place, a combination of magnetic and electrostatic separation can be used to further process the ore. Due to the fact that monazite and xenotime are paramagnetic, magnetic separation can be used to further concentrate the minerals by removing rutile and zircon. Furthermore, magnetic gangue such as magnetite can also be removed using this method (Ferron et al., 1991). Electrostatic separation, on the other hand, works on the basis of particle sizes and ion conductivity. They are used when the other methods prove insufficient. It can be used in minerals which have similar specific gravities and magnetic properties to gangue, such as in the case of xenotime and monazite (Jha et al., 2016).

Flotation is another important method used in beneficiation and is widely used when dealing with fine grained deposits where gravity separation proves ineffective (Jordens et al., 2013). It relies on the surface chemistry of minerals and the electrical double layer they form, utilizing a collector to adsorb them under specified conditions (mainly pH and temperature) (X. Zhang, Du, Wang, &

Miller, 2013). This collector then rises to the top of the reactor. Common collectors for monazite include fatty acids and hydroxamates. However, as Jordens et al. (2013) mentioned monazite sands contain rutile and zircon, both of which prevent the selective flotation of monazite. Due to this, depressants like sodium silicate and sulfite are used to inhibit the co-adsorption of these minerals. The exact mechanisms of monazite surface chemistry behaviour for the case of flotation is still widely debated and requires further study. All of these methods have been used in order to beneficiate monazite. Further detail about beneficiation of Monazite sands can be found in Jha et al. (2016).

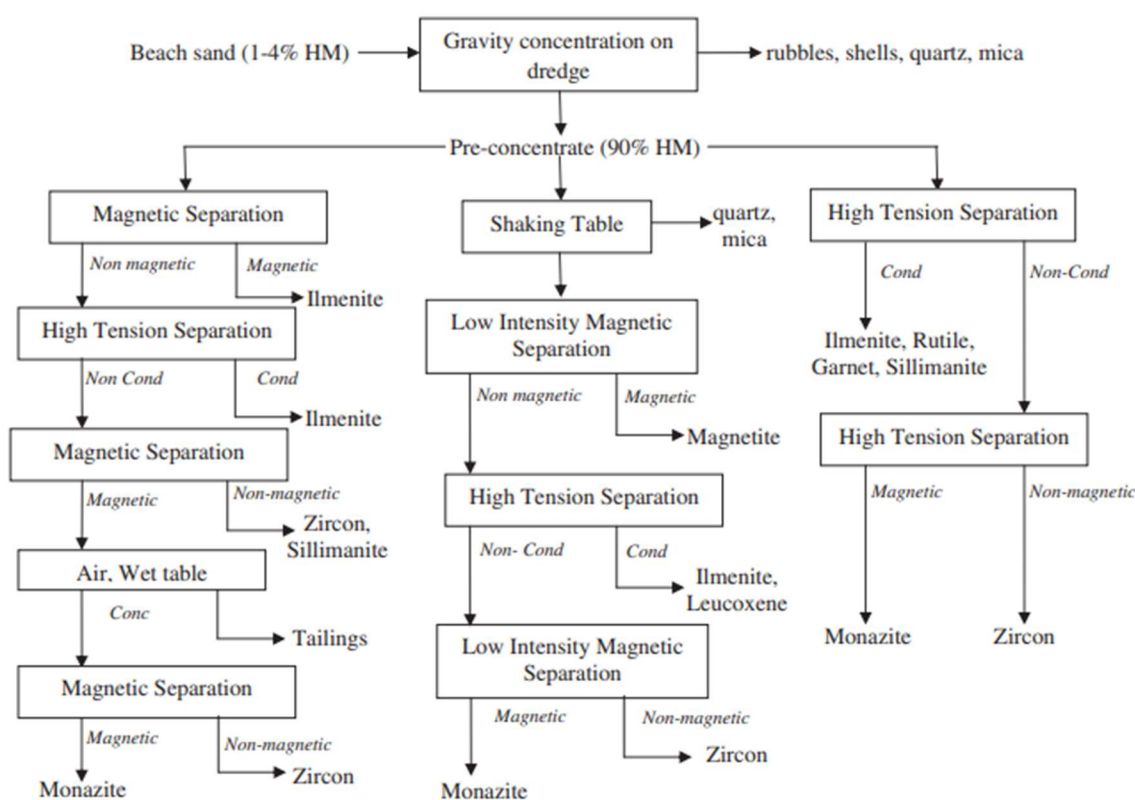


Figure 2.1: Beneficiation methods of monazite taken from B. Gupta, Malik, and Deep (2002)

2.1.2 Extraction

Rare earths concentrates can be recovered using two methods which are either through wet digestion or chlorination (Fathi Habashi, 1997). Of these, by far the most common method is wet digestion. The current processes for rare earth extraction usually focus on the

decomposition/digestion of rare earth minerals followed by leaching. These wet methods are either hydrometallurgical processes or usually a combination of hydrometallurgical and pyrometallurgical processes (Jha et al., 2016). Hydrometallurgical processes involve using a reagent (usually an acid or base) to leach REEs from their corresponding ore. Pyrometallurgical processes, on the other hand use heat-based methods for purification. Another notable branch of hydrometallurgy in REE extraction, is biohydrometallurgy. However, it is deemed outside the scope of this study. The type of process used can vary with the minerals present, the grade and the end products required (Jack Zhang, Zhao, & Schreiner, 2016). The monazite concentrate can be leached in a suitable reagent either directly or after digestion.

2.1.2.1 Direct Leaching

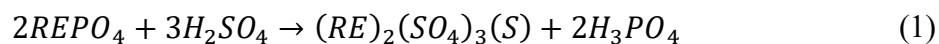
As hypothesized previously, monazite concentrate exists as a stable, crystalline structure and therefore harsh conditions are required in order to break it down efficiently (E. Kim & Osseo-Asare, 2012). Various direct leaching methods have been studied by the scientific community and will be evaluated in this section.

2.1.2.1.1 Acid Leaching

2.1.2.1.1.1 Sulfuric Acid

By far the most extensively used method of acid leaching, is the sulfuric acid treatment. The sulfate ion (SO_4^{2-}) behaves as a ligand and forms complexes with the REEs at high temperatures. This makes sulfuric acid superior to other acids, which primarily rely on proton attack (Borrowman & Rosenbaum, 1961).

The equation for the reaction is as follows:



The basis for direct acid leaching with sulfuric acid is outlined in E. Kim and Osseo-Asare (2012). The paper uses Pourbaix diagrams to compare the REE- PO_4 - H_2O environment with the REE- PO_4 - SO_4 - H_2O environment in monazite. It hypothesizes that most naturally occurring monazite exists in a stable crystalline form and demonstrates that the metals in crystalline monazite are

thermodynamically stable in acidic conditions. However, the addition of the (SO_4^{2-}) ion helps shrink the stability domains of these phosphate regions (Figure 2.2, Figure 2.3) favoring the formation of the soluble sulfates of Ce, La and Nd. Increasing the concentration of (SO_4^{2-}) further increases the solubility domains (Figure 2.4). The paper also demonstrates that the solubility of the sulfates formed also decrease at high temperatures and has been a basis for of cold-water dissolution of the aforementioned sulfates.

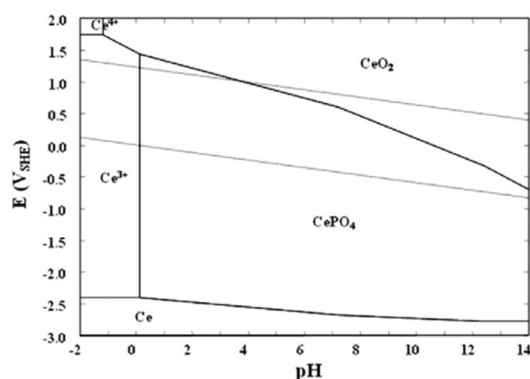


Figure 2.2: Eh-pH diagram for crystalline Ce-PO₄-H₂O systems at 25C, (E. Kim & Osseo-Asare, 2012)

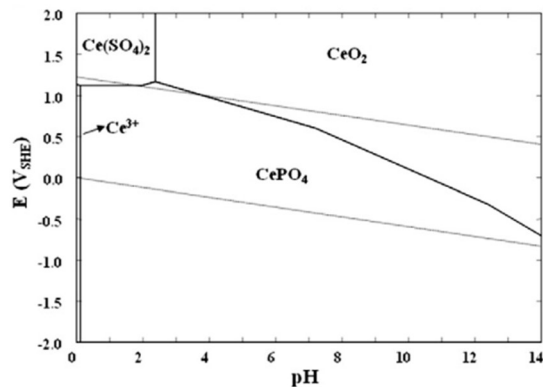


Figure 2.3: Eh-pH diagram for crystalline Ce-PO₄-SO₄-H₂O systems at 25C at $[\text{SO}_4] = 10^{-2}\text{M}$, (E. Kim & Osseo-Asare, 2012)

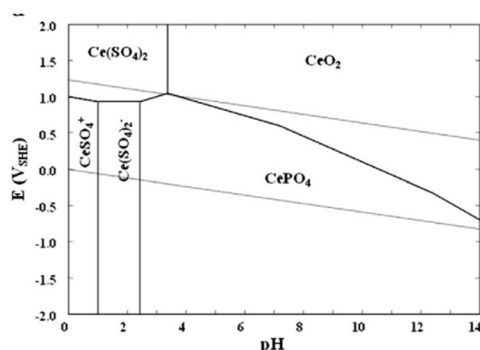


Figure 2.4: Eh-pH diagram for crystalline Ce-PO₄-SO₄-H₂O systems at 25°C at [SO₄] = 1.0 M, (E. Kim & Osseo-Asare, 2012)

The sulphuric acid leaching process commonly involves using a prior step of acid decomposition. The most traditional method of the sulfuric acid treatment is digestion for 2-4 hours at 200-250°C at a 1.5:1 liquid-to-solid ratio followed by cold water leaching in order to obtain a sulfate solution, which could then be precipitated using oxalic acid (Barghusen & Smutz, 1958; Borrowman & Rosenbaum, 1961). This process has been modified over the years and the digestion step has been adapted to be either high (>300°C) and low temperature (<300°C). Low temperature decomposition allows for 90% dissolution of REEs and is suitable for lower grades of monazite (Borrowman & Rosenbaum, 1961) but concentrates, soluble impurities become an issue and must be treated (J. Zhang et al., 2016). The high temperature decomposition allows for quantitative leaching of REEs but one of the main impurities is Th which tends to form a soluble sulfate under 300°C but can form insoluble ThP₂O₇ at higher temperatures. Furthermore, at temperatures of 650-800°C, monazite reforms and REE extraction decreases. Therefore, methods to increase REE solubility at high temperatures are currently being evaluated (Demol et al., 2018). Recently Demol, Ho, Soldenhoff, Karatchevtseva, and Senanayake (2022) completed the baking method in the presence of iron oxides/hydroxides in order to accomplish this. Furthermore, Outotec developed a method to recover SO₂ gas during high temperature treatment and convert it to H₂SO₄ using patented fluidized bed technology (Sadri, Nazari, & Ghahreman, 2017). Sadri et al. (2017) also mentions that Search minerals in Vancouver has also developed a process to only use coarse crushing (saving energy on fine crushing and grinding) followed by H₂SO₄ digestion at 200°C to produce water soluble sulfates, after which the solution is neutralized and treated with Na₂CO₃ to precipitate REE carbonates which can be leached with HCl.

S. Chen et al. (2020) conducted a study on the kinetic behaviour of direct leaching of sulfuric acid roasted Batou mixed bastnasite and monazite concentrate, analyzing the effect of acidity, particle size, temperature and liquid-solid ratio and concluded that REEs and P leaches far quicker than Fe. This indicates that leaching solutions could be made purer by reducing the leaching time as phosphate breakdown occurs quicker than iron extraction.

Shin, Park, and Yoo (2012) compared various methods of direct sulfuric acid leaching of monazite on lanthanum and cerium extraction. The pressure leaching conducted at 5 atm, 200°C and 5% pulp density showed a linear correlation between sulfuric acid concentration and extraction. Smaller particle sizes also lead to increased extraction. The paper also analysed the effect of temperatures between 50-225°C and concentrated sulfuric acid in the atmospheric pressure leaching of Ce, La and Nd, displaying a steady increase in extractions up to temperatures of 150°C. After this there was a slower increase, with over 99% of the Nd and La extracted at 220°C, and only 60% extraction of Ce. It is important to note that high temperature leaching produced a paste that required cold water dissolution. These experiments demonstrate the importance of sulfuric acid concentration and temperature on extraction efficiency.

Common problems with the sulfuric acid method involve the formation of impure products (C. K. Gupta & Krishnamurthy, 1992) and harsh conditions, typically requiring high concentrations of toxic sulphuric acid in addition to high temperatures. Despite this, the method remains important, still being used by the world's largest REE producer for processing the Batou mixed bastnasite/monazite (Z. Zhang et al., 2015). There are also a host of other companies opting for the method such as the Sarfartoq method in Greenland (Goode et al., 2013) and companies like Hastings and the Lynas corporation (Demol et al., 2018).

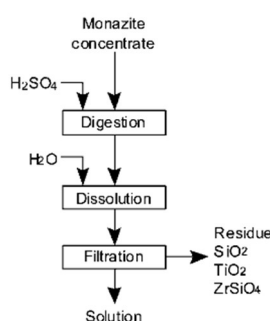


Figure 2.5: Example of the sulfuric acid process in industry after (Fathi Habashi, 1997)

2.1.2.1.1.2 Nitric Acid

Lin, Yang, Werner, and Honaker (2021) constructed Eh-pH diagrams in 1M HNO₃ and concluded that soluble Ce(III) can be formed stably under pH, 3.5. However, the experiments conducted showed extremely poor extraction percentages for Ce. Therefore, it was hypothesized that the crystallinity of naturally occurring monazite require more energy than those in the HSc software and can therefore result in low cerium extraction values. Furthermore, the lack of a ligand attack can slow the kinetics of the reaction. Moreover, Pourbaix diagrams for Nd and La, show that they are insoluble unless high acid concentrations are used. This could result in formation of Nd and La surface films preventing further leaching. HNO₃ is also a known oxidant and can result in the formation of Ce(IV) which can precipitate within the solution (Bandara & Senanayake, 2015).

The leaching of phosphate rock (containing apatite and monazite) using nitric acid was researched by Aly and Mohammed (1999), (Jorjani, Bagherieh, & Chelgani, 2011) and (Stone, Bandara, Senanayake, & Jayasekera, 2016). Apatite in particular was shown to be effectively leached using nitric acid, with acidity, temperature, solid-liquid ratio and time all playing a factor in REE extraction. Bunuş and Dumitrescu (1992) also concluded that nitric acid leads to higher solubility of REEs in sedimentary REE containing phosphates compared to the wet sulfuric acid treatment. Phosphate rock is decidedly easier to breakdown without a ligand attack but does contain extremely low proportions of REO.

Kuzmin, Pashkov, Lomaev, Voskresenskaya, and Kuzmina (2012) developed a method to leach low concentration REO mixtures (containing phosphate in the form of monazite and florensite) from deposits in Russia. Due to high iron content in these ores, sulfuric acid was shown to be unsuitable due to high consumption (Sadri et al., 2017) so the method used nitric acid at elevated temperatures, which was shown to increase recovery. Temperatures of greater than 140°C reduced dissolution of iron into the leachate. Models were used to demonstrate the possibility of sorbing phosphoric acid in the iron oxide, and forming solid hydroxy ferric phosphates, potentially explaining a way to also reduce the phosphate content in the leachate. This process achieved 87-90% recovery of REEs and the resulting leachate was treated with Na₂CO₃ to produce REE carbonates which underwent further processing. The nitric acid could also be recovered in this process.

B. Gupta et al. (2002) also successfully dissolved monazite using a combination of HNO_3 , HF and HClO_4 (at 3:1.5:0.5) in 24 hours at 80°C . However, the test only used 0.1g monazite.

Bujnovskij, Sachkov, Molokov, and Anufrieva (2016) investigated direct nitric acid leaching of a man-made monazite deposit under high pressure. Temperatures of 453K, 473K and 693K were used and shown to only weakly increase REE recovery. However, nitric acid concentration and time were major factors in improving dissolution. The optimum conditions were found to be 9M HNO_3 , 150 minutes and 473K, to achieve a recovery of 55-60% REE. This method was investigated due to the fact that REE nitrate solutions can be easily extracted and refined using TBP, so the direct production of a nitrate leachate would greatly simplify the extraction and refining process (Rabie, 2007).

El-Nadi, Daoud, and Aly (2005) treated the oxide cake of monazite sand treated by alkali treatment in order to completely leach out REE hydroxides.

2.1.2.1.1.3 Hydrochloric Acid

Similar to HNO_3 treatment, Ce extraction under 1M HCl showed poor extraction values despite the ion stability displayed in Eh-pH diagrams (Lin et al., 2021). Once again this was attributed to high crystallinity, a lack of ligand to attack and formation of insoluble layers.

Not much research exists on direct leaching of monazite using HCl . Archana Kumari, Jha, Hait, Sahu, and Kumar (2013) investigated a two-step direct leaching method for a Korean monazite concentrate using HCl . The dissolution was shown to increase with acid concentration, temperature and time but plateaued after a certain period. The first stage was shown to recover only 25% REEs at optimum conditions of two hours, 100 g/L and moderate temperatures. When the residue was re-leached under the same conditions, the REE extraction went up to 45%.

Shin et al. (2012) used an electrogenerated chlorine leaching using HCl under $40\text{mA}/\text{cm}^2$ current density, 5% pulp density for two hours to extract REEs. Temperature was found to play a large role in REE extraction.

2.1.2.1.1.4 Other Acids

Watts and Fisher (2021) avoided the need for long reaction times and fine grinding of particles seen during H_2SO_4 , HCl , HNO_3 and NaOH leaching by using condensed phosphoric acid to achieve

greater than 99% extraction of light rare earths at 260°C within just 30 minutes. An additional benefit of the system was that phosphoric acid is milder than the aforementioned reagents.

Bandara and Senanayake (2015) studied the leachability of monazite containing fluorapatite, using HCl, HNO₃, HClO and H₃PO₄. HClO₄ showed a far higher REE extractions (51-64%) compared to HCl and HNO₃ where the leaching efficiencies were 13-21% and 5-7% respectively. In the case of H₃PO₄, La, Ce and Nd extraction peaked to 60%, 40% and 25% respectively within 10 minutes before plummeting to less 20%. All reagents peaked at 10 minutes after which there was increased precipitation in the solution.

Daniel E. Lazo, Dyer, Alorro, and Browner (2017) used various organic acids to leach monazite. Citric acid, maleic acid and oxalic acid at pH=2 produced the highest phosphorus dissolution. Oxalic acid at pH=2 was shown to produce the highest breakdown of phosphates in the monazite but exhibited low REE dissolution, indicating reaction conversion rather than direct dissolution. Oxalic acid was further tested in an attempt to increase the monazite conversion. Increasing the oxalic acid concentration from 0.2M to 1M further increased phosphate dissolution but seemed to have no impact on REE leaching, which bolstered the assumption that REE phosphates are converted to another insoluble species. Increasing other parameters, similarly, had little to no effect on REE extraction. Therefore, it was concluded that the REEs underwent conversion to insoluble oxalates. This study shows a lot of promise into the future of monazite leaching as it indicates that greener acids can act to successfully leach monazite.

2.1.2.1.1.5 Comparison of Acids

In addition to the ligand attack, H₂SO₄ remains a preferred reagent for acid leaching compared to the other inorganic acids due to its lower cost; in addition to the high volatility of HCl and high decomposability of HNO₃ which can result in toxic gases emitted to the atmosphere (X. Yang & Honaker, 2020). It is important to note that all three of these forms of acid leaching require fine grinding of monazite particles and can take long periods of time. Archana Kumari et al. (2013) showed a potential advantage of the HCl treatment is the formation of solid RECl₃ along with the H₃PO₄ allowing the phosphate to be recovered. The monazite and RECl₃ residue could be re-leached in dilute HCl to dissolve the rare earth chlorides.

Lin et al. (2021) conducted direct leaching tests of monazite with all three inorganic acids and concluded that HNO_3 and HCl both performed better than H_2SO_4 . Furthermore, the curve for extraction with sulfuric acid leaching appeared to flatten with time, while that of HNO_3 and HCl both showed a gradual increase in extraction. However, these tests were conducted at room temperature in low acid concentration (1M) and resulted in recoveries of $<0.8\%$ within the two-hour time period. HNO_3 was shown to perform marginally better than HCl . This result was corroborated by Stone et al. (2016).

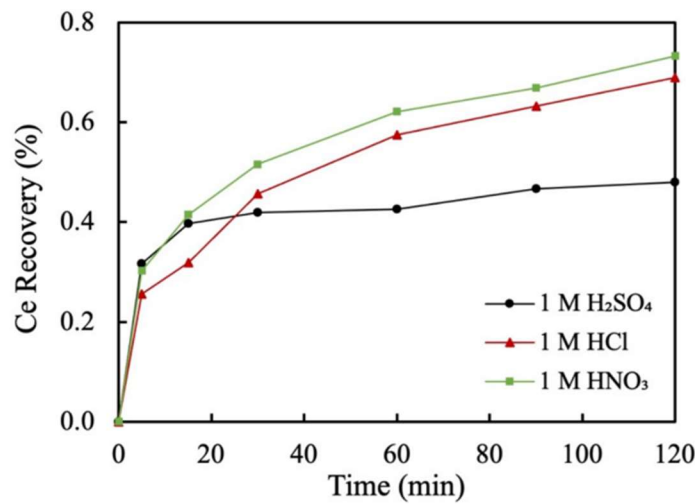
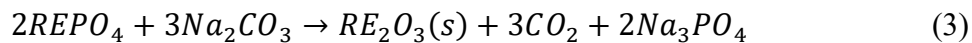


Figure 2.6: Comparison of Ce recovery with time with different acids after (Lin et al., 2021)

In another study comparing thermodynamics of inorganic acids in the direct acid leaching of monazite; HCl was found to have the lowest activation energy compared to HCl and H_2SO_4 (Azizi, 2018).

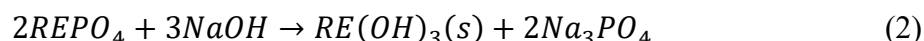
2.1.2.1.2 Alkaline Leaching

Alkaline treatment began by using caustic soda (Na_2CO_3) at high temperatures and pressures to dissolve the phosphates and obtain the by-product Na_3PO_4 , which can be used in the fertilizer industry (C. K. Gupta & Krishnamurthy, 1992; J. Zhang et al., 2016). At temperatures between $600\text{-}700^\circ\text{C}$, the following REE reaction took place (Sadri et al., 2017).



The caustic soda process is still used in Malaysia and France (C. K. Gupta & Krishnamurthy, 1992; Sulaiman, 1991).

NaOH has since come into the forefront of alkaline leaching. Using concentrated 70% NaOH at 150°C for two hours was found to produce insoluble RE and Th hydroxides, breaking down the phosphates in solution (F. Habashi, 2013; Jha et al., 2016). The reaction also produces sodium triphosphate. The reaction proceeds as follows:



J. Zhang and Edwards (2013) found that increasing the concentration of NaOH from 50% to 60% reduced the leaching time from five hours to just one hour. El-Nadi et al. (2005) and S.-D. Kim, Lee, Kim, Yoon, and Kim (2010) studied the optimization conditions for this method and found an optimum mole ratio of 15 and time of two hours. Panda et al. (2014) achieved 99.9% dephosphorization of using 50% NaOH for four hours at 60g/L with a Korean monazite.

Both the Na₂CO₃ method (C. K. Gupta & Krishnamurthy, 1992; Sulaiman, 1991) and the NaOH methods (Jha et al., 2016; Sulaiman, 1991) are still used in the industry with the NaOH method preferred due to higher REE recovery. However, the caustic soda method leads to less thorium remaining in the REE residue (C. K. Gupta & Krishnamurthy, 1992).

A disadvantage of the NaOH dissolution is the significant consumption of the NaOH and the difficulty in filtering the jelly mass formed (Panda et al., 2014). Another interesting development was to combine grinding and NaOH leaching steps to allow the mechanochemical formation of Rare-earth hydroxides (Abdel-Rehim, 2002; W. Kim, Bae, Chae, & Shin, 2009).

Potassium hydroxide (KOH) was also evaluated instead of NaOH (A. Kumari et al., 2019) and was found to produce good recoveries at a 1:1 ratio and temperatures of 250°C in just 30 minutes.

The solid REH produced during these alkaline processes cab to further processing to leach the REEs with acids. This is discussed in 2.1.2.3.

2.1.2.2 Pre-treatment

A number of studies have been undertaken to investigate the effects of pre-treating the monazite prior to leaching. This is due to the thermal and chemical stability of the phosphate structure in monazite (A. Kumari et al., 2019). Therefore, dephosphorization of monazite is considered an important factor in efficient extraction of REEs.

The sulfuric acid and sodium hydroxide methods are such methods and have been discussed in previous sections but there are other methods such as the roasting of the ore with alkalis (Jha et al., 2016). Examples of such alkali materials are CaO, NaCl-CaCl₂ or KOH (Azizi, 2018). An advantage of this method is reduction of time for monazite decomposition, in addition to avoiding high energy fine grinding methods. However, recoveries are shown to be lower than conventional methods (Azizi, 2018).

Xing, Zhuang, Tu, and Guo (2010) investigated the dephosphorization of monazite with charred coal and found high efficiencies between 1200-1400°C. When the monazite was molded into pellets with water and charred coal, 98% dephosphorization was achieved at 1400°C for two hours. Udayakumar et al. (2020) reported a high rate of dephosphorization with carbon at 1450°C and a monazite: carbon mole ratio of 0.7.

Shuchen et al. (2007) used CaO and 10% NaCl-CaCl₂ to decompose 79% of phosphates in monazite in one hour. Wu, Bian, Wu, Sun, and Tu (2007) studied the calcination of a mixed bastnasite-monazite mineral using a CaO-NaCl-CaCl₂, showing that monazite decomposition occurs between 610-700°C, with 90.8% decomposition occurring at 700°C.

S.-D. Kim et al. (2010) managed the decomposition of phosphates at 460°C and a 6:1 mole ratio of NaOH:REEOH while A. Kumari et al. (2019) found that using KOH at 250°C at a 1:1 ratio proved to be effective. Purwanti, Setyadji, Astuti, Perdana, and Petrus (2020) analysed the NaOH decomposition of an Indonesian monazite to achieve optimal conditions between 300-600°C and a 1:1 ratio.

B. Zhang, Xue, Yang, and Ri (2019) attempted to reduce alkali dosage during roasting, by mixing the NaOH with Ca(OH)₂, obtaining positive results at 800°C for 1.5 hours with 20% Ca(OH)₂ and 25% NaOH. Abdel-Rehim (2002) used alkaline ball-milling methods to decompose phosphates. The grinding action of the steel balls allowed for the removal of the hydroxide layer on the surface

of monazite grains. Mechanical methods were also thought to improve the breakdown of the phosphate crystal (E. Kim & Osseo-Asare, 2012). Huang, Zhang, Liu, Dou, and Tian (2016) investigated the use of microwave in order to aid in the alkali decomposition of phosphates. Microwave was shown to lower the decomposition temperature compared to that of conventional heating.

An advantage of the roasting technique to pre-leach the ore, is a lower consumption of alkalis and less issues with subsequent filtration (A. Kumari et al., 2019) compared to direct alkali leaching.

Daniel E. Lazo et al. (2017) investigated the use of organic acids for phosphate breakdown of monazite, with oxalic acid at pH 1.3 releasing approximately 30% phosphates in the system in 10 hours. The REEs formed precipitated as a solid oxalate salt. D. E. Lazo, Dyer, Alorro, and Browner (2018) continued the investigation and found that the P release was directly linked to REE extraction. However, REE extraction was often higher than P release which was possibly thought to be due to reprecipitation or adsorption of P. Furthermore, temperatures of 65°C was found to achieve the optimum breakdown, where temperatures of 85°C led to lower values. They stated that this was due to competing oxalate consumption of iron under higher temperatures. While these numbers are significantly worse than conventional methods, the use of clean organic acids and ambient temperature give them great potential for future research. Rashad, kassab, Fathy, and El Sheikh (2021) used citric acid to extract 94% of uranium from alkaline pretreated monazite.

2.1.2.3 Leaching after pre-treatment

The solids formed from the roasting and pre-treatment methods require dissolution in order to proceed to the separation steps. There are numerous studies analysing this.

Franken (1995) investigated a sulfuric acid roast leach process. This process involved a conversion of REE phosphates to REOs and used a stepwise selective solubilisation to leach with acids. The Ce was first solubilized at 427°C and leached with sulfuric acid. The temperature was then further increased for selective solubilization of other rare earths like Nd and La. The study also found that HCl was found to be a better leaching agent than both H₂SO₄ and HNO₃ during the process, and sonication was shown assist the leaching procedure.

HCl appears to be used to extract REEs from alkaline de-phosphorized monazite in a number of studies. J.-S. Kim, Yoon, Kim, Kim, and Lee (2004) used 8N HCl for two hours at 10% pulp density and 80°C to extract 90% REEs from an ore decomposed using caustic soda. Both E. Kim and Osseo-Asare (2012) and S.-D. Kim et al. (2010) used 6N HCl to leach a NaOH treated ore and also achieved 90% REE extraction. Meanwhile, Panda et al. (2014) heated NaOH and treated monazite to convert the oxides to hydroxides and leached the solid using dilute HCl at 90°C for two hours to extract 95% of REEs. A. Kumari et al. (2019) also used a 1M HCl and 10% v/v H₂O₂ solution for 120 minutes for REE extraction of an ore treated with KOH.

Huang et al. (2016) used 3N HCl at 20:1 liquid to solid ratio to extract 93% of REEs after microwave alkaline decomposition of monazite.

The use of nitric acid was seen in a study by Ali, El-Nadi, Daoud, and Aly (2007) where 4M HNO₃ was used to dissolve an ore that had been treated with NaOH. The treated ore was first washed with a Na₂CO₃, NaOH and H₂O₂ mixture in order to first remove the uranium prior to dissolution using HNO₃. As mentioned previously nitric acid leaching solutions are easier to extract downstream with TBP(Rabie, 2007).

W. Kim et al. (2009) used sulfuric acid to extract REEs after mechanochemical treatment of monazite with NaOH in a ball mill. 0.05N H₂SO₄ was shown to achieve greater than 85% extractions of La, Nd and Sm displaying selectivity compared to Ce and Pr which was 20% and 70% respectively. This was due to conversion of Ce and Pr into their respective oxides which only dissolved once the H₂SO₄ concentration was increased to 5N.

D. E. Lazo et al. (2018) published a paper evaluating the effect of organic acids on monazite that had been pretreated with oxalic acid. The monazite concentrates (combination of oxalate and phosphate) formed in the first step was subjected to an alkaline leach under multiple acids. EDTA was found to be the most effective and selectivity was shown towards the extraction of Nd. A maximum single pass extraction was achieved in five minutes at a pH of 10 under ambient conditions. The REEs could then be converted to REE Hydroxides for downstream processing.

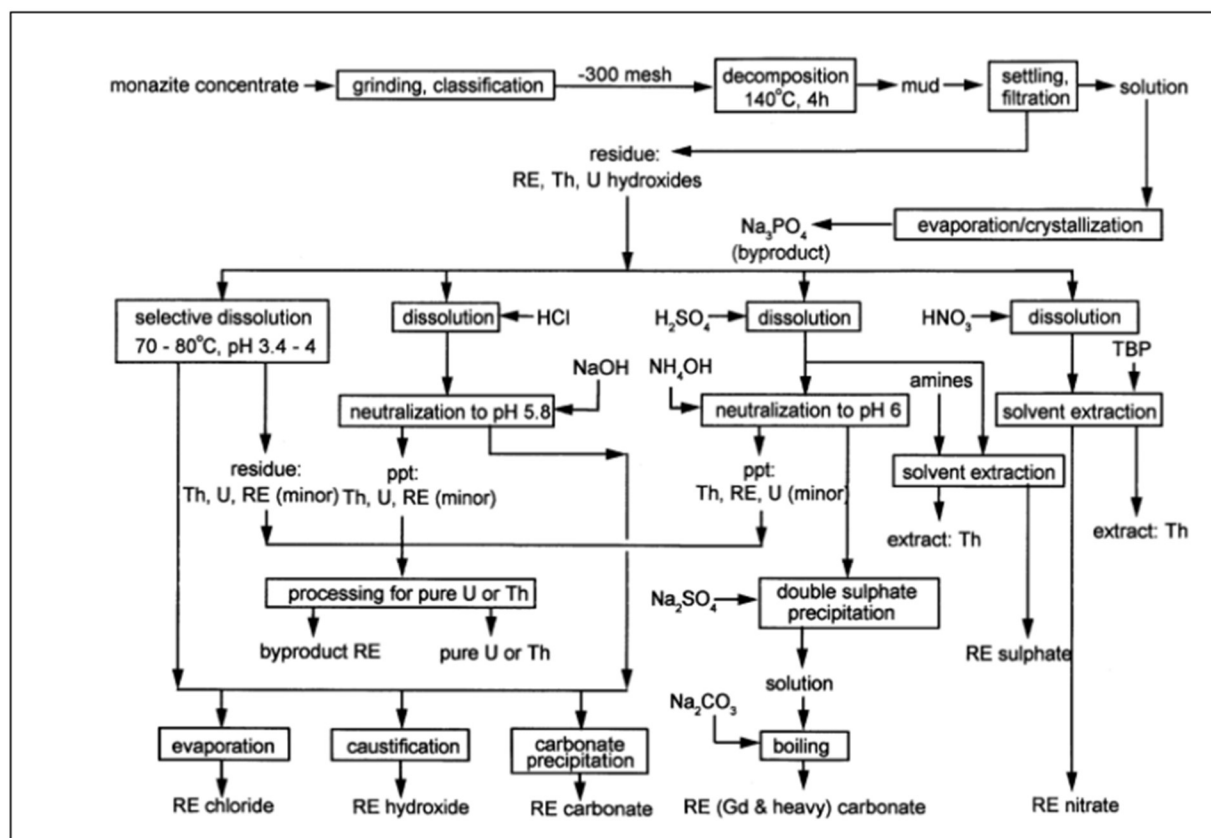


Figure 2.7: Treatment of pretreated ores taken from Azizi, 2018

Despite a number of methods being researched in monazite extraction, the NaOH and H₂SO₄ method remain the most industrially used ones and therefore, improvement of methods utilizing these reagents is highly desired.

2.1.3 Further processing

The leach solution of monazite containing the mixture of REEs and other metals are then separated using Solvent Extraction and/or precipitation. Both methods have been reviewed in literature (Jha et al., 2016), but a quick summary is provided below.

2.1.3.1 Solvent Extraction

In the case of Solvent Extraction of sulfate liquors, REEs, Th and U have historically been extracted using amine extraction, where the amine type strongly affected the separation (Crouse, 1959). Th and U, on the other hand have been removed using di-n-octylamine (DoA) and trybutylamine

(TBA). Rabie, Abdel-Wahaab, Mahmoud, Hussein, and Fatah (2013) used Tributylphosphate (TBP) to completely remove U from sulfate liquor, after which the resulting solution was stripped using cold water. Primene JM-T and Alamine 336 in kerosene has also been used to almost completely extract Th and U selectively, from sulfate liquors. These were then stripped using HCl (Amaral & Morais, 2010).

In the case of chloride solutions, many different extractant types have been researched. Cationic extractants of organophosphorus acids like D2EPHA and HEHEHP have been used. HEHEPs such as Lonquest 80, P-507, SME 418, EHEHPA have been preferred to D2EHPA as they can be stripped at lower acidities. The extraction order for EHEHPAs favours Y and other HREEs over LREEs, Dy, and Tb. Dy can then be separated similarly in the second step of the extraction (Singh, Kotekar, & Singh, 2008). Another such extractant is PC 88A, which has been used to fractionate LREEs in three groups of La-Ce-Pr-Nd, Sm-Gd-Eu and Y-heavy rich fractions. The Sm-Gd-Eu fraction could further treated with saponified PC 88A to obtain 95% pure Sm. The same can be done for the first fraction to pure Nd. The Ce in the first fraction could also be precipitated using sodium hypochlorite to achieve 90% pure cerium hydroxide. PC 88A can then be used again to extract Ce from the hydroxide after treatment with HNO_3 . Meanwhile, the La, Pr and other impurities remaining in the SX solution can be precipitated as carbonates and the HREEs dissolved using HCl. The solution, containing 50% La, could be purified to 99.9% by using PC-88A to extract the HREEs (Thakur, 2000). Cyanex-272 is the only di-alkyl phosphonic acid used in industry.

Carboxylic acids have also been used for REE extraction in literature. Naphthenic and Versatic acids in have been promising in extracting Y with other REEs. Y showed similar extraction coefficient to HREEs in D2EPHA solutions but were similar to LREEs in Versatic and Naphthenic acids (Zheng, Gray, & Stevens, 1991). However, the presence of the naphthenic acid can hinder the process due to its high solubility resulting in reagent losses. Less soluble carboxylic acids such as CA-100 and CA-12 have been developed in order to combat this issue. Other promising extractants include chelating extractants and anionic extractants such as Primene JMT and Aliquat 336.

B. Gupta et al. (2002) used Cyanex to remove U, Th and Ce,Y-lanthanides from a leach solution containing HNO_3 , HF and HClO_4 . D2EHPA has been used to separate Sm, Eu and Gd from other REEs in nitric-hydrochloric acid solution, achieving 78% recovery. Mixtures of Cyanex 301 and

Cyanex 903 were also reportedly effective in extracting REEs from nitrate solutions (Reddy, 1977). Aliquat 336 is also effective in extracting LREEs from HREEs in nitrate media (Preston, 1996).

2.1.3.2 Precipitation

REEs could also be fractionally precipitated as sulfates, bromates and oxalates. Abreu and Morais (2010) used precipitation to purify REEs as $\text{Na}(\text{RE})(\text{SO}_4)_2 \cdot x\text{H}_2\text{O}$. These were then converted to $\text{RE}(\text{OH})_3$ using NaOH. Ce(III) easily oxidizes to its tetravalent form Ce(IV) in alkaline solutions, or in the presence of strong oxidants in acidic solutions. The Ce(IV) is insoluble and so the soluble trivalent REEs could be selectively dissolved. KMnO_4 is one such oxidant, and the oxidation process results in the precipitation of $\text{Ce}(\text{OH})_4$ and MnO_2 . The mixture can then be dissolved in HCl, and further precipitated using oxalic acid or ammonium hydroxide before finally calcining the precipitate to obtain 99.5% pure CeO_2 .

More information on Solvent Extraction and Precipitation of REE from solution could be obtained in (Jha et al., 2016).

2.2 Sonication

The previous section highlighted various complications in the current methods to extract REEs from monazite. Therefore, searching for better techniques to minimize these drawbacks need to be found and evaluated. The use of ultrasound as an auxiliary form of energy has been increasingly studied over the past few years and has been shown to improve leaching processes (Swamy et al., 1995).

The following section will aim to provide an understanding to the basics of ultrasound followed by a thorough evaluation of the use of sonication in leaching with a focus on selected relevant works.

2.2.1 Sonication Theory

Ultrasound refers to soundwaves higher than the range of human hearing, which is 16 KHz. According to Swamy et al. (1995), , “the upper limit of ultrasound leaching is approximately 5 MHz for gases and 500 MHz for liquids and solids”. Ultrasound uses can be divided into low power, high frequency (1-10 MHz) and high power, low frequency (20-100KHz). The former is used for diagnostics while the latter is used to produce physical and chemical changes in materials and can be used for leaching, cleaning and facilitating other chemical reactions. Abed (2002) shows a summary of the sonic spectrum below:

Table 2.1: Sonic spectrum and uses from (Abed, 2002)

Range	Frequency	Category	Uses
Human hearing	16-18 KHz		
Conventional ultrasound	20 -100 KHz	High Power – Low frequency	Leaching, cleaning
Sonochemistry	20 KHz – 2 MHz	High Power – Low frequency	Synthesis
Diagnostic ultrasound	5 – 10 MHz	Low Power – High frequency	Fetal development

Cavitation occurs when the bubbles formed by negative pressures overcome the attractive forces of molecules in the liquid medium. The distance between molecules in water is approximately 10^{-8} cm and the applied pressure is enough to overcome the surface tension (σ), which is around 10.1×10^5 Pa according to the equation 4 (Vernès, Vian, & Chemat, 2020):

$$P_c = \frac{2\sigma}{R} \quad (4)$$

This can lead to hot spots, which are regions of high temperature ($>5000\text{K}$) and pressure (100MPa) created by the collapse of these bubbles. The ultrasound effects can be attributed to these local hotspots and the subsequent shockwaves they formed by the implosion, which can create large shear forces. The low energy sound waves are concentrated into intensely energy dense regions (Abed, 2002; Swamy et al., 1995).

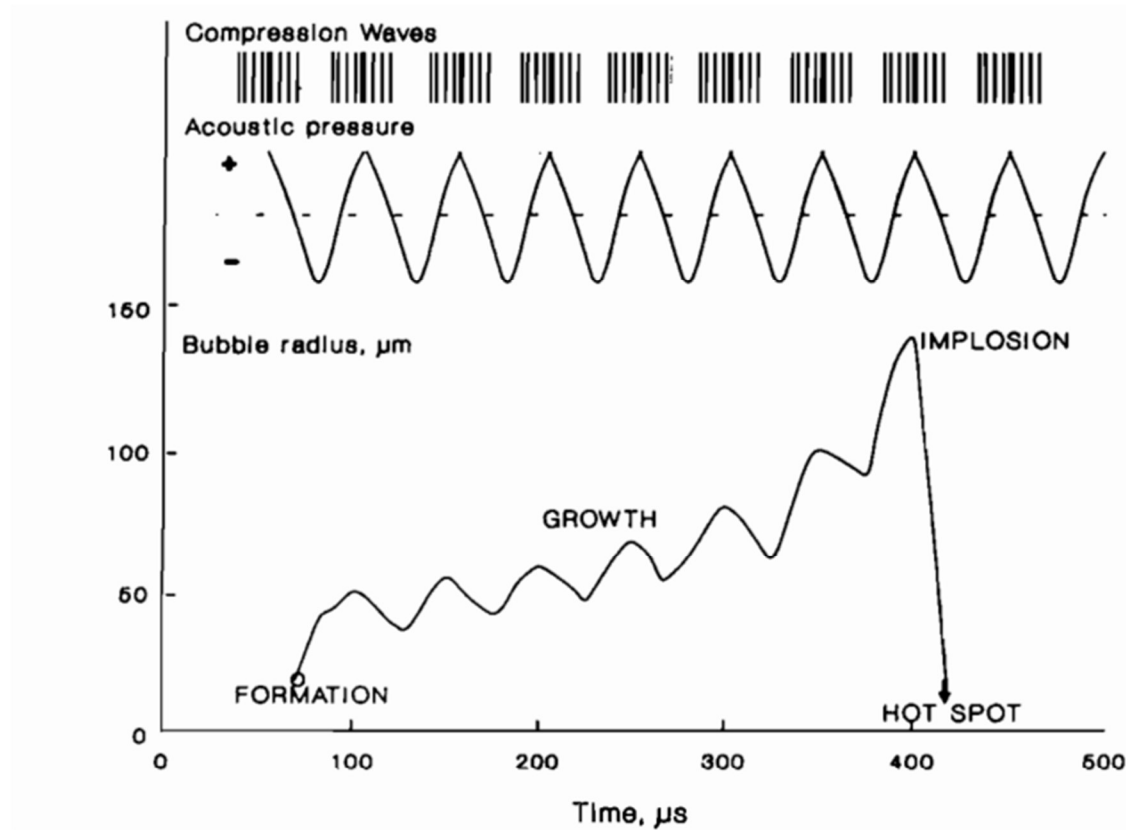


Figure 2.8: Cavitation Bubble Dynamics taken from Gupta (2002)

Cavitation is most effective when nucleation sites are already present, due to local inhomogeneities and can also occur through previous cavitation cycles. Cavitation can be termed stable when the bubble oscillates through many acoustic cycles, causing micro-streams. They contain more gas and only collapse less violently compared to transient cavitation. Transient cavitation only exists for a few cycles, where the bubble radius rapidly expands and causes violent implosion. This limited time frame is thought to prevent mass transfer through the bubble liquid interface and the resulting decrease in cushioning is believed to intensify the implosion (Ashokkumar et al., 2009; Mason & Lorimer, 1988). There are various expressions describing acoustic pressures required to generate transient bubbles under different properties (Holland & Apfel, 1990; T. Leighton, 2012).

2.2.1.1 Bubble Dynamics

The effects of ultrasound are largely as a consequence of bubble dynamics. The Rayleigh-plesset equation describes the response of a gas bubble in a liquid driven by a variable pressure field (Ensminger & Bond, 2011; T. G. Leighton, 2008). This can be used to determine stable cavitation growth rates:

$$\ddot{R}R + \frac{3\dot{R}^2}{2} = \frac{1}{\rho_o} \left(p_L - \frac{4\eta\dot{R}}{R} - p_\infty \right) \quad (5)$$

Where ρ_o and η represent the bulk liquid density, shear viscosity respectively. $\dot{R}$ and $\ddot{R}$ represents the first and second order derivative of the bubble radius with respect to time.

p_∞ represents liquid pressure at a distance from the bubble and is defined by:

$$p_\infty = p_0 + p(t) \quad (6)$$

The polytropic gas law, in conjunction with relations for surface tension (σ) and vapour pressure p_v , can be used to describe liquid pressure (p_L) at the bubble wall:

$$p_L = \left(p_0 + \frac{2\sigma}{R_0} - p_v \right) \left(\frac{R_0}{R} \right)^{3\kappa} + p_v - \frac{2\sigma}{R} \quad (7)$$

Where R_0 is the undisturbed bubble radius and κ is the polytropic index.

To finally get:

$$\ddot{R}\dot{R} + \frac{3\dot{R}^2}{2} = \frac{1}{\rho_o} \left[\left(p_0 + \frac{2\sigma}{R_0} - p_v \right) \left(\frac{R_0}{R} \right)^{3\kappa} + p_v - \frac{2\sigma}{R} - \frac{4\eta\dot{R}}{R} - p_0 - P(t) \right] \quad (8)$$

Transient cavitation growth rates can be modelled by (T. Leighton, 2012):

$$R\ddot{R} + \frac{3\dot{R}^2}{2} = \frac{1}{\rho_o} \left(P \left(\frac{R_{max}}{R} \right)^{3\kappa} - P_m \right) \quad (9)$$

Where R_{max} is the radius of the bubble prior to collapse and P_m is the corresponding liquid pressure.

The resulting conditions due to transient cavitation collapse can be described by:

$$T_{max} = T_0 \left[\frac{(P_m(\gamma - 1))}{P} \right] \quad (10)$$

$$P_{max} = P \left[\frac{(P_m(\gamma - 1))}{P} \right]^{\frac{\gamma}{\gamma-1}} \quad (11)$$

$$\frac{R_{min}}{R_{max}} = \left[\frac{P}{P_m(\gamma - 1)} \right]^{\frac{\gamma}{3(\gamma-1)}} \quad (12)$$

Where T_{max} , P_{max} and R_{max} represent the maximum conditions prior to transient collapse and R_{min} is the minimum (which is greater than the nucleation radius). γ is the ratio of specific heats (C_p/C_v) within the bubble and can be defined as unity in isothermal conditions like the growth of the bubble.

2.2.1.2 Cavitation

The chemical effects of ultrasound in high power, low frequency systems occur due to acoustic cavitation. Ultrasound waves lead to molecular vibrations in liquids which cause cycles of compression and rarefaction. Cavitation occurs when the intermolecular forces of a liquid are unable to hold the molecule together during rarefaction, forming low pressure cavities. This nucleated bubble expands over the following acoustics cycles (during the rare faction) as vapour fills the bubble until it finally implodes.

Properties affecting cavitation are outlined in Vernès et al. (2020) and Meroni, Djellabi, Ashokkumar, Bianchi, and Boffito (2022):

1. **Solvent properties like viscosity, saturation vapour pressure and surface tension:**
High viscosities mean more intermolecular interactions, which therefore need more energy to cavitate. Meanwhile, increasing vapor pressure and surface tension tend to reduce cavitation effects.
2. **Temperature:** In addition to being a key variable in defining vapour pressure, temperatures near boiling point allow more cavitation bubble formation, albeit with lower implosion capacity.
3. **Acoustic frequency:** High acoustic frequencies lead to shorter rarefaction phases, adversely impacting cavitation as bubble formation is more unlikely. Low frequencies cause fewer cavitation bubbles than higher frequencies, but these bubbles are larger in size and can therefore lead to increased intensity of cavitation collapse.
4. **Acoustic intensity (Power):** The acoustic power is directly related to the amplitude pressure of the wave. Increasing this increases the size and number of cavitation bubbles. It is important to provide the power required to obtain the cavitation threshold pressure. The power required for this is also dependant on solvent properties such as viscosity. Optimum power values for cavitation could be possible due to over formation of bubbles leading to attenuation of the energy transfer.
5. **Pressure in medium:** Cavitation bubbles are generated when the sum of acoustic and hydrostatic pressures of the system are less than the saturation vapour pressure.

6. **Dissolved gases:** Dissolved gases act as initiation sites for cavitation and if a reagent is degassed, nucleation of bubbles are diminished, decreasing cavitation effects. Gas bubbling of inerts like argon can act to reduce the heat dissipation in a medium as the maximum collapse. Temperatures are dependant on thermal conductivity of the gases in the solutions. Therefore, argon can enable higher temperatures for collapsing.
7. **Surfactants:** Surfactants can act to reduce the coalescing of bubbles as they can adsorb at the bubble-liquid interface and result in smaller cavitation bubbles.

While there have been some investigations into bubble dynamics (Ashokkumar, 2011; Ashokkumar et al., 2009; Holland & Apfel, 1990), further explanation is deemed outside the scope of this project.

2.2.1.3 Ultrasound devices

There are a variety of ultrasound devices, but they all are composed of a generator and a transducer. The generator converts electricity from the main line frequency to ultrasonic frequencies. The transducer converts this to ultrasonic waves using acoustic vibrations which can be transmitted using horns or plates. Transducers can be of various types such as piezo-electric, capacitive, electrostatic or magnetostrictive. Piezo-electric and magnetostrictive, however remain the most common (Ensminger & Bond, 2011).

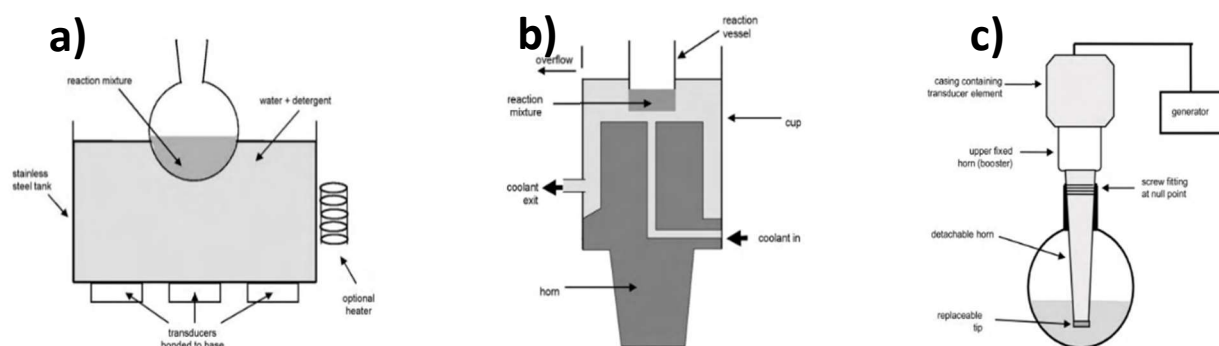


Figure 2.9: Sonication systems: a) Bath type, b) Probe type c) Cup-horn type taken from (Ensminger & Bond, 2011)

Piezoelectric transducers use ceramic piezoelectric components that oscillate under the influence of an electric field. Magnetostrictive transducers change dimensions under a magnetic field and so

are usually made of iron and nickel wrapped around a copper coil, which generates a magnetic field when electrical current is applied. Piezoelectric components are usually smaller, less expensive and more efficient as electrical charge can directly be converted to mechanical energy while magnetostrictive material require a prior conversion of electrical to magnetic energy. However, magnetostrictive transducers can operate under higher temperatures (Abed, 2002; Ensminger & Bond, 2011).

There are three main set ups for sonication: the ultrasonic bath, the cup horn and the probe horn system as shown in Figure 2.9. The probe horn is a method of direct sonication and was found to be most effective in multiple studies (Diehl, 2018; Ratoarinoro, Wilhelm, Berlan, & Delmas, 1992) while the bath was found to be the least effective.

The ultrasonic bath produces low intensities and uneven effects of sonication. Its results are difficult to reproduce as there are many factors such as sample position, US intensity, and liquid level, that affect the sonication. However, they are cheap, provide an even distribution of energy, easily available and suitable for cleaning applications.

The cup horn is another indirect form of sonication where an inverted horn is placed at the bottom of the system and sonication occurs through a cooling solution irradiating into a solution held in a closed reactor. These are known to have better frequency control, in addition to control over sample atmosphere. They can also mitigate radical formation (Abed, 2002; Suslick, 2000).

However, the most widely used method of sonication remains the sonotrode, where a probe is directly inserted in the reaction medium. The cavitation occurs most intensely under the tip of the horn and can provide vigorous mixing. They offer flexibility catering to various power requirements and can even operate under moderate pressures. The acoustic intensities are also reproducible as the acoustic frequencies are usually fixed at 20KHz. A disadvantage of this system is the erosion of the tip which can lead to contamination of the reaction mixture in addition to requiring constant replacement of the probe tip (Suslick, 2000).

There are many producers such as Hielscher and Sonics and materialsTM with a lot of entry potential for new companies as there is lots of research in minimizing energy use while maximizing the cavitation impact with little damage to the probe.

The erosion of the probe occurs due to the simultaneous behaviour of chemical attack and cyclic stress leading to shorter fatigue life. Even at ambient conditions corrosion can occur, with pitting being a commonly seen issue in materials. This is when pits form on material surfaces due to chemical reactions with the surface. These pits become nucleation sites for cracking, which, once formed are further propagated by the corrosive environment. These effects can be somewhat diminished by increasing the load application frequency so that the crack is exposed to the environment for shorter periods of time. Other methods include application of surface coatings, selecting corrosion resistant materials and reducing the corrosivity of the environment (Ensminger & Bond, 2011).

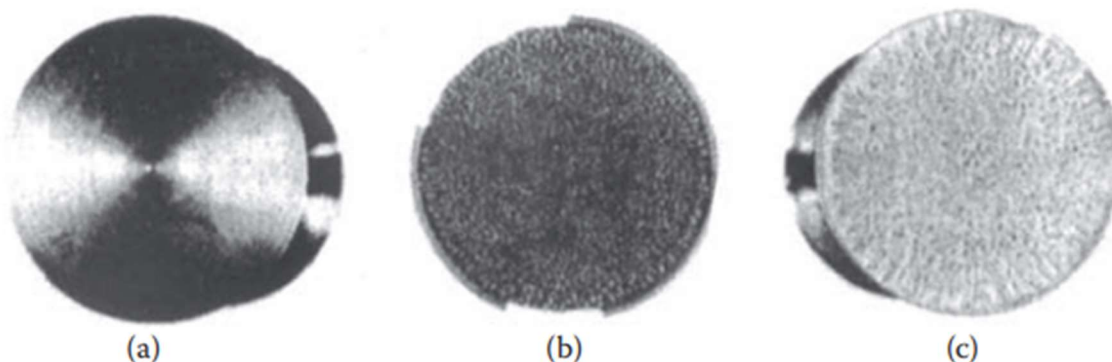


Figure 2.10: Sonotrode under various levels of erosion: a) unused, b) moderately use and c) heavy use after (Ensminger & Bond, 2011)

Another limitation of sonotrode systems is that common horns produce cavitation at localized spots near its tip. This can lead to difficulties in obtaining reproducible results and issues with scale up. To combat this, specialized shapes of probe have been developed. One such example is the cascetrode, designed by Hielscher. This is designed to have discs along the neck of the sonotrode resulting in multiple active reactive zones. Many other different shapes of sonotrode are being designed (Meroni et al., 2022).

2.2.1.4 Acoustic Power

The equation for sonic energy and its dependence on frequency can be described by (Abed, 2002):

$$\theta = \frac{2\pi^2 f^2}{\rho c} \left[\frac{4}{3} \eta_s + \eta_B + \frac{(\gamma - 1)\kappa}{C_p} \right] \quad (13)$$

Where f is the ultrasound frequency, ρ is the bulk medium density and c is the ultrasonic velocity in the medium. η_s and η_B represent the shear and bulk viscosities of the medium, respectively while C_p is the specific heat of reaction mixture. Furthermore, γ is C_p/C_v and κ is Boltzmann's constant. This shows the relationship between ultrasound frequency and properties of the medium.

Ultrasound waves transfer in a liquid medium transfer their energy within the medium, increasing its temperature. Therefore, calorimetric methods could be used to quantify the energy efficiency of the system (Contamine, Wilhelm, Berlan, & Delmas, 1995) and give an indication of power used in cavitation. The calorimetric equation is as follows (Meroni et al., 2022):

$$P_{diss} = mC_p \left(\frac{dT}{dt} \right) + (m_i c_{pi} \Delta T) + (hA\Delta T) \quad (14)$$

The “ m ” in the first term represents the mass of solution being sonicated. The second term is used to calculate the energy lost by the reactor and transducer as conduction and the final term accounts for convection losses to ambient air.

In most studies, the second and third terms are neglected, due to negligible losses of the other terms, and the equation can be reduced to:

$$P_{diss} = mC_p \left(\frac{dT}{dt} \right) \quad (15)$$

The intensity of this dissipated power can be further calculated by (Vernès et al., 2020):

$$I_{diss} = \frac{P_{diss}}{A_{probe}} = \frac{4P_{diss}}{\pi D_{probe}^2} \quad (16)$$

In sonotrode systems, the input power has been found to be dependent on horn height and depth, and also proportional to the input power of the system (Kimura et al., 1996). Qsonica™ mentions that running a probe at a certain amplitude in air and subtracting that from the power delivered in

a sample provides a good idea of the power being delivered to that sample but the energy absorbed by the system depends on amplitude, physiochemical properties and reactor geometry. Therefore, it is important to calibrate the intensity curves for a certain medium in order to determine the sonic power transmitted to a solution. Calorimetry is the most effective method to determine the power dissipated in a solution.

Acoustic intensity, “I”, decreases as distance from probe increases. It’s variation with frequency, “f”, is given by the equation:

$$I = 0.5\rho CA^2f^2 \quad (17)$$

Where “A” stands for the amplitude of vibrations. The amplitude of a sonication probe indicates the total it moves longitudinally during vibration. The maximum amplitude differs between probes and many newer probe systems contain settings that allow control of the system as a percentage of the maximum amplitude.

The amplitude of a probe is proportional to its intensity (W/cm² probe) from equation 17, and therefore, the delivered intensity in a particular solution is the most crucial factor for reproducibility of ultrasound experiments. Reproducibility of ultrasound results during sono-chemical research depends on a number of parameters such as medium viscosity and reactor volume. Therefore, the best method to display experimental results is using Intensity (Power/mL) in a certain medium rather than just power. This is also useful for scale up of experiments.

It is also important to note that increasing the acoustic power also increases the number and size of bubbles formed during cavitation, in addition to increasing the amount of chemically active bubbles through radical formation.

When ultrasonic powers in a medium is too high, the resultant sono-chemical yields can be drastically lowered due to attenuation caused by bubble cloud formations which absorb sound waves. This is known as shielding. Another reason for decreased yields is known as decoupling losses, which means the increased bubbles associated with high powers decrease the energy transfer from the ultrasound sources (Meroni et al., 2022).

2.2.2 Sono-chemical leaching

Ultrasound in leaching has been widely studied over the years, with its effects of leaching coming into focus in recent years. As mentioned previously, leaching is a combination of solubility and transport phenomena, and the use of ultrasound has been proven to enhance those mechanisms. The effects of ultrasound can be attributed to both physical and chemical effects.

The chemical effects of ultrasound are thought to be due to the generation of free radical species, which are created by high temperatures and pressures after cavitation collapse. These free radicals can allow chemical reactions to proceed, forming intermediates (Ameta, 2018). At lower frequencies associated, the collapse of larger bubbles result in higher temperatures, which in turn lead to formation of more free radicals. However, total radical yield is higher at high frequencies as more bubbles are formed. There is an upper limit to this as extremely high frequencies cause a reduction in cavitation. Furthermore, radical formation is currently associated primarily with homogeneous liquids (Meroni et al., 2022) but has been speculated in a number of leaching experiments.

Free radical formation proceeds as follows (D. Zhang et al., 2017):



In recent literature on leaching, free radicals have been strongly linked to oxidising potential in various media, altering reaction mechanisms (Gui, Hu, Wang, & Zhang, 2022; Gui, Wang, & Zhang, 2021a; Toache-Pérez, Bolarín-Miró, De Jesús, & Lapidus, 2020; Zhu, Zhang, Li, Qian, & Zhou, 2012).

In heterogeneous systems, the effects of sonochemistry are largely physical. Suslick (2000) concluded that these effects are due to a combination of improved heat and mass transfer, surface activation, and solid liquid interface. This can be further explained by a variety of mechanisms. Microstreaming can cause erosion of solid surfaces, thereby activating surfaces and removing passivating layers. Transient cavitation also leads to extremely high localized temperatures and pressures that can generate large shear forces that both intensify the aforementioned effects and cause violent collisions, in addition to the formation of microjets that propagate toward nearby surfaces leading to pitting, erosion and other morphological changes.

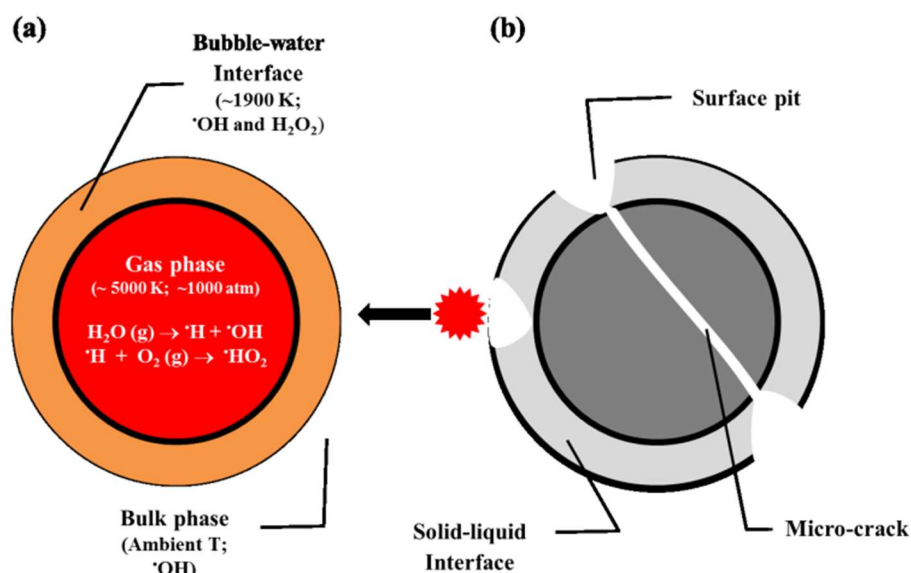


Figure 2.11: Effects of cavitation after (Wei, 2015)

Swamy et al. (1995) decoupled the mechanical effects attributed to increased specific surface area with other possible physical effects and concluded that reaction rates do increase due to improved mass transfer. Increased specific surface area occurs as the particle breaks down into smaller pieces that are more accessible to the leachate. The reduction in boundary layer thickness and the increase in active surface area increase the mass transfer rate and more indirectly, the reduced viscosity of the solvent during sonication, increases the mass transfer co-efficient, which further increases mass transfer rates.

The equations are given below:

$$Rate = \frac{K_d A_p C_o}{\pi} \quad (24)$$

Where K_d is the mass transfer coefficient, and C_o is the initial solvent concentration while A_p is the total surface area of the particles and π is the thickness of the liquid boundary film. π is known to decrease with agitation, which could occur from both mechanical stirring and sonication.

K_d is expressed as follows:

$$K_d = \frac{D}{d} \left[2 + 0.4 \left(E^{\frac{1}{4}} * \frac{d}{D^{\frac{1}{3}}} * \frac{\rho_L^{\frac{5}{12}}}{\mu_L^{\frac{1}{12}}} \right) \right] * f \quad (25)$$

Where D is the diffusivity of the corresponding reagent in the solvent, while d is the average particle diameter while E is the ultrasonic power dissipated per unit mass of liquid and μ_L and ρ_L are the viscosity and density of the liquid, respectively.

Therefore, it is reasonable to assume that ultrasound breaks down particles and causes a decrease in particle size, increasing the active surface area and thus, the reaction rate. Furthermore, the equation shows that ultrasound increases the mass transfer coefficient by decreasing the viscosity of the solution. Finally, the boundary layer thickness also decreases due to ultrasound, therefore increasing the mass transfer rate.

In conclusion, ultrasound is thought to have three primary effects on solid-liquid leaching:

1. Increased active surface areas
2. Improved heat and mass transport rates
3. Affect the oxidation potentials of reaction systems

While research on sono-chemical leaching of rare earths remains limited, the sono-chemical leaching of metals has been intensively researched over the past few years. While Swamy et al. (1995) and Abed (2002) have provided a comprehensive review of this in the early 2000s, a literature review of recent developments in sono-chemical extraction remains limited. Therefore, the next few pages will focus on this.

2.2.2.1 Iron and Copper

The removal of the iron coatings in silica sands has been historically widely researched. Iron impurities tend to attach to the surface of quartz or embed themselves in it and can be difficult to remove using traditional methods. Farmer, Collings, and Jameson (2000) used sonication to treat silica sand with sodium carbonate and found that it worked better than attrition methods. Ultrasound power was shown to be the factor that impacted the results as opposed to total ultrasonic work done, due to its ability to separate the forces adhering the finer coatings to quartz. The ultrasound effect was attributed primarily to particle collisions rather than other factors such as changing the S/L ratio was shown to have little effect on the reaction. H. L. Zhao, Wang, Cai, and Zhang (2007) showed that ultrasound washing of silica sand with reagents like Na_2CO_3 , Na_2SO_3 and AlCl_3 was much more effective than conventional scrubbing methods. These reagents were used to prevent aggregation of the particle. Du, Li, Li, and Zhang (2011) used oxalic acid and ultrasound to extract 94.5% of the iron in 50 minutes (compared to 87.4% in 80 minutes without ultrasound). The oxalic acid was shown to have a synergistic effect when combined with ultrasound, allowing better breakdown of particles compared to water. Furthermore, ultrasound allowed lower concentrations of oxalic acid to be used in achieving better results. C.-Q. Yang and Li (2020) found that ultrasound led to faster leaching time of iron from quartz while the kinetics were shown to be diffusion controlled both with and without ultrasound. Interestingly, activation energy was shown to be higher with the use of ultrasound (27.7 KJ/mol vs 20.44 KJ/mol) which is different from other literature about ultrasound Yoon (2017), which mention a decrease in apparent activation energy.

Brunelli and Dabalà (2015) analysed the application of ultrasound in Zn furnace dust in order to separate the iron from zinc furnace dust containing franklinite. Ultrasound was shown to greatly improve zinc recovery. Low concentrations of H_2SO_4 were shown to selectively extract zinc as the acid was consumed more efficiently, resulting in an increased solution pH, thus precipitating iron hydroxides. X. Li, Xing, Du, Gao, and Chen (2017) used ultrasound to remove iron from boron carbide waste scraps. Ultrasound was shown to decrease agglomeration, in addition to peeling the particle surface and removing iron from both the surface and the iron embedded within the particle. This was due to improved diffusion and constant access to fresh reactive surfaces. Increasing

ultrasound frequency was shown to decrease iron removal which attributed to less violent cavitation at higher frequencies.

For copper leaching, recent literature has attempted to reduce acid use. Yoon et al. (2017) used acidic FeCl_3 and ultrasound to leach chalcopyrite. Ultrasound was shown to improve the extraction of copper by 10%. The rate limiting step using ultrasound was only ash layer diffusion compared to a combination of product and ash layer diffusion without ultrasound. J. Wang, Faraji, and Ghahreman (2020) used acidic ferric sulfate and ultrasound to improve chalcopyrite extraction with ultrasound removing the passivation layer on the surface. Lower pulp density displayed improved ultrasound effects, attributed to reduced viscosity and cavitation.

Beşe (2007) used sulphuric acid ferric sulfate mixtures with ultrasound to achieve improved extraction of copper, zinc, cobalt and iron from copper converter slag while Turan, Sari, and Demiraslan (2019) investigated greener methods of copper slag treatment, using H_2O_2 and acetic acid with ultrasound in order to selectively extract copper (93%) while minimizing the iron extraction (3%).

Another interesting paper involving both copper and iron was Xie et al. (2009), where H_2SO_4 , H_2O_2 and ultrasound were used to selectively extract copper over iron from printed circuit board waste sludge. Ultrasound was thought to increase the ion movement and prevent formation of insoluble $\text{Fe}(\text{OH})_2$ on the surface of soluble $\text{Cu}(\text{OH})_2$, facilitating dissolution in addition to enhancing settlement of the insoluble iron hydroxides. Higher ultrasound powers allowed for higher separation between the two.

It is important to note that most of the papers above have used SEM to demonstrate a combination of particle size decrease, increased breakage, increased active surface areas and removal of passivating films.

Table 2.2: Iron and Copper sonication literature

System Studied	Reagents	Ultrasound system	Notable findings	Reference
Silica Sands – Fe coating removal	Na_2CO_3	Probe type	1. Sonication worked better in removing the iron coating than attrition 2. The effect of ultrasound was attributed to particle collision 3. Higher power led to improved results, compared to work – attributed to separation of fine coatings that adhered	(Farmer et al., 2000)
Silica Sands – Fe coating removal and comparison to scrubbing	Washing with water and comparison of washing between: • Na_2CO_3 • Na_2SiO_3 • $(\text{Na}_3\text{PO}_3)_6$ • AlCl_3	Designed system: Tank connected to six ceramic transducers	1. Sonication was more effective than just scrubbing: Up to 52.7% removal of iron efficiency with water in 10 minutes (45% improvement over scrubbing) 2. Replacing turbid water with fresh water improved results 3. Adding chemicals prevented aggregation and led to a further 15-30% improvement over pure water 4. Na_2SiO_3, Na_2CO_3 and AlCl_3 were the most effective	(H. L. Zhao et al., 2007)
Silica Sands – Iron removal	Oxalic Acid	Probe type	1. Sonication improved Fe removal 2. 75.4% iron removal under optimum conditions of: 95°C, 500 rpm stirring, 150W ultrasound power, 4gpl oxalic acid, 30 minutes 3. Increasing ultrasound power improved the results 4. Ultrasound was shown to work synergistically with oxalic acid to remove coatings of particles	(Du et al., 2011)
Quartz – Iron removal, kinetic analysis	$\text{H}_2\text{C}_2\text{O}_4\text{-HCl}$ solution	Probe type	1. Iron removal increased with temperature, stirring speed and ultrasound power 2. Maximum iron removal of 74% achieved in 40 minutes with ultrasound (compared to 8 hours under silent conditions) 3. Shrinking core model, product layer internal diffusion-controlled leaching step 4. Activation energy increased under sonication was 27.72 KJ/mol (an increase of 7.28 KJ/mol under silent conditions)	(C.-Q. Yang & Li, 2020)
Electric arc furnace dust – Fe and Zn removal by dissolving frankinite	H_2SO_4	Probe type	1. Sonication improved Zn recovery under all investigated conditions 2. Fe recovery was lower than conventional under concentrations of 0.5M H_2SO_4 3. 0.5M H_2SO_4 (low concentration) was deemed the most effective as it allowed 59% Zn recovery but allowed for the reprecipitation of Fe, facilitating selectivity 4. Higher acid concentrations improved Zn recovery but reduced the selectivity 5. Selectivity attributed to acid consumption at low concentrations increasing the pH and allowing precipitation of Fe.	(Brunelli & Dabalà, 2015)
BC_3 waste scrap – iron leaching	H_2SO_4	Bath type	1. 94.5% Fe removal in 50 minutes (compared to 87.4% in 80 minutes in silent conditions) 2. The sonication method shows 2-stages of rate determining steps, first reaction controlled and second diffusion controlled (compared to chemical reaction controlled under silent conditions), attributed to ultrasound affecting extraction from both surface of the particle and within	(X. Li et al., 2017)

			3. Ultrasound led to decreased agglomeration of particles, peeling due to cavitation and decrease in mass transfer resistance 4. Increasing the frequency decreased extraction, attributed to less violent cavitation 5. Sonication increased the rate of reaction, shortened the time and lowered the iron in the residue	
Poorly soluble CuFeS ₂ – Copper leaching	FeCl ₃ -HCl solution	Probe type	1. 87% Cu recovery (compared to 77% in silent) under optimized conditions of: 20g/L pulp density, 0.01M FeCl₃, 0.1M HCl, 500 rpm, 50-99°C, 5W power 2. Ash layer diffusion-controlled step under sonication compared to ash and sulfur product layers under silent conditions 3. Apparent activation energy of 32 kJ/mol under sonication (compared to 33kJ/mol): attributed to removal of sulfur layer using ultrasound, allowing easy penetration for FeCl₃	(Yoon et al., 2017)
CuFeS ₂ - oxidative copper leaching	FeCl ₃ -H ₂ SO ₄ solution	Probe type	1. 57.5% Cu recovery (compared to 50.5% in silent) under optimized conditions of: 1% S/L, 0.5M Acid, 80°C, 20% amplitude power 2. The effects on leaching were temperature>ultrasonic power>S/L ratio>acid concentration 3. Reaction time reduced from 5 hours to 4 hours under sonication 4. Diffusion and chemical controlled in both methods 5. Sonication was shown to increase leaching rate, shorten reaction time and reduce acid consumption 6. Particles more loose and porous particles under sonication 7. The pre-exponential factor tripled under sonication 8. Improvements attributed to: Increased particle breakage and removal of sulfur product layer	(J. Wang et al., 2020)
Copper slag from converters	Fe ₂ (SO ₄) ₃ -H ₂ SO ₄ solution	Probe type	1. Ultrasound enhances dissolution of Cu, Zn, Co and Fe 2. 89.2%, 51.32%, 69.87%, 13.73% of Cu, Zn, Co and Fe (compared to 80.41%, 48.28%, 64.52% and 12.16% under silent conditions) in optimized conditions for copper dissolution of: 65°C, 0.2M H₂SO₄, 0.15 Fe₂(SO₄)₃, 180 minutes	(Beşe, 2007)
Blended copper slag – Selective copper removal	H ₂ O ₂ +Acetic Acid	Probe type	1. 93% Cu dissolution and 3% Fe dissolution under optimized conditions of: 2M H₂O₂, 4M CH₃COOH, 10% ultrasound amplitude power, 65°C, 60 minutes, 1:1.25 S/L ratio 2. Optimum conditions provided selectivity for Copper and Zinc over Iron 3. Increasing ultrasound power, increased extraction 4. Ultrasound method two times faster than magnetic stirring 5. Ultrasound shown to create microcracks on particle surface 6. Increase BET surface area	(Turan et al., 2019)
Printed Circuit Board (PCB) waste sludge – Selective copper removal	H ₂ SO ₄ +H ₂ O ₂ – 2 methods of addition 1. High H₂O₂ slurry added to High H₂SO₄ slurry 2. H₂SO₄ added to H₂O₂ slurry	Tank connected to transducers connected to generator with variable power	1. 97.83% and 1.23% under optimized conditions of: 3.0 final pH, 25°C initial temperature (increased due to ultrasound), 160W, 60 minutes 2. Cu leaching showed: Ultrasound (25°C)> Conventional (80°C)> Conventional (25°C)	(Xie et al., 2009)

while Fe leaching showed: Conventional (25°C)
Conventional (80°C) > Ultrasound (25°C), which
indicated good selectivity

3. Method 1 better for selectivity due to
heterogenous crystallization of iron at smooth
pH increase from 1.5 to 3 compared to regions
of high acid concentration in method 2 which
results in colloids
4. Fe leaching inhibition attributed to formation of
large Fe crystals under sonication, which then
settle

2.2.2.2 Gold and Silver

Due to the increasing demand for gold refractory ores have become increasingly important in recent times. However, they are difficult to leach due to sulfide passivation layers and are therefore a good candidate for ultrasound extraction.

P. Zhu et al. (2012) used electro chlorination and ultrasound. Ultrasound time ratio was shown to increase the extraction of gold, compared to mechanical stirring. The paper also mentioned an increase in activation energy using ultrasound but showed no comparison of a test without ultrasound. Fu, Zhang, Wang, Cui, and Peng (2017) used alkaline NaClO to obtain the extraction of gold in two hours using ultrasound compared to six hours without it. Extraction improved as ultrasound power was raised from 50W-200W due to increasing cavitation but sharply dropped after due to possible decomposition of NaClO and lower cavitation effect due to formation of coalescing bubbles. G. Zhang, Wang, Zhang, and Peng (2016) pretreated a refractory ore with NaOH and ultrasound followed by NaCN leaching with ultrasound. The paper showed that lower pre-treatment times facilitated higher extract subsequent leaching step. This was attributed to the FeS₂ in the ore reacting with SiO₂ in the ore to form increasing amounts of NaSiO₄ over time, which in turn absorbs gold. Ultrasound was shown to increase gold extraction during the acid leaching steps but higher powers of 1KW lead to a decomposition of NaCN due to reaction with H₂O₂ formed from free radicals during ultrasound. Notably, the ultrasound power was found to be the most important factor during orthogonal experiments. P. Guo, Wang, and Zhang (2019) selectively removed antimony using ultrasound and alkaline Na₂S to enable more effective alkaline NaClO leaching. Ultrasound was used in both steps and drastically improved both the antimony removal and the gold leaching. It also required lower temperatures to achieve better and faster results. The kinetics showed that the gold leaching was reaction controlled and ultrasound improved the frequency factor. Ultrasound also resulted in small uniform particles compared to conventional leaching. Gui, Wang, and Zhang (2021b) evaluated the impact of ultrasound on refractory ores by testing the breakdown of pyrites (main component of refractory ores) with H₂O₂ and potassium thiocyanate. Ultrasound damaged the pyrite crystal structure and Fe₂O₃ deposits were stripped while more OH radicals were formed as ultrasound power increased facilitating the oxidation of Fe²⁺ to Fe³⁺ which catalytically oxidised the reaction. Gui et al. (2022) used ozone and sodium cyanurate under ultrasound to improve the leaching of gold and silver from refractory ores.

Ultrasound prevented the agglomeration of particles and prevented an iron oxide/hydroxide layer. Increased ultrasound power led to more reactive ozone and rapidly improved extraction efficiencies.

Yu et al. (2020) used ultrasound and barren liquor with NaCN makeup to treat gold concentrate at low temperatures. Ultrasound reduced leaching time to 4 hours at 10°C (from 24 hours at 25°C) and reduced CN^- consumption by 15% due to these lower temperatures. Pores and fissures were visible on the treated particles due to microjets while particle size was also much smaller than the conventional treatment. Ultrasound was also used by Gui, Khan, Wang, and Zhang (2020) to improve the leaching of gold concentrate by thiosulfate and cobalt ammonia, leading to 25% higher extraction percentages that was eight times faster than conventional mixing. When the kinetics of the reaction was evaluated, it was interesting to note that the while both methods were diffusion controlled, the system become less diffusion controlled and more reaction controlled as ultrasound power was increased which agrees with the theory of ultrasound improving diffusion. The activation energy decreased from 22.65 KJ/mol to 13.86 KJ/mol using ultrasound.

Öncel, Ince, and Bayramoğlu (2005) used thiourea and ultrasound to extract silver from silver ore processing solid waste. Ultrasound was shown to form hydroxide radicals that oxidised silver sulfides in the ore.

Table 2.3: Gold and silver sonication literature

System Studied	Reagents	Ultrasound system	Notable findings	Reference
Refractory gold - Kinetics	HCl+Cl ₂	Bath type	- Gold leaching ratio increases with time ratio (stirring vs sonication), initial HCl concentration and temperature - Diffusion controlled reaction where ultrasound decreases diffusion resistance and has no product layer on unreacted surface	(P. Zhu et al., 2012)
Refractory gold – chlorination oxidation	NaClO+ NaOH	Probe type	68.55% gold extraction under optimal conditions of: 1.5M NaClO, 1.5M NaOH, 5 S/L ratio, 200W power 2 hours (vs 45.8% in 6 hours under silent conditions) - Sonicated particles displayed peeling of interface layer exposing fresh surface - Ultrasound power was shown to be the most important factor affecting gold leaching - Powers of over 200W resulted in decreased extraction, attributed to decomposition of NaClO and shielding effects of cavitation overpower	(Fu et al., 2017)
Refractory gold	2 steps: - Pretreated with NaOH + sonication - Leached with NaCN + CaO with and without sonication	Cup horn type	- Low pre-treatment times of 1 hour led to higher leaching ratios and lower NaOH concentrations led to higher leaching ratios. Both of these were attributed to the formation of NaSiO₄, which absorbs gold - Ultrasound leaching increases gold extraction - Increasing ultrasound power upto 180W achieves 73.4% gold extraction after 5 hours (compared to 40.3% in silent conditions) - Increasing ultrasound power further up to 1KW in 5 hours decreases gold recovery – attributed to decomposition of CN⁻ 1 KW ultrasound power is more effective than 120W and 180W within the first two hours - The maximum Au recovery observed in the investigation was 80.7% under conditions of: 3 hours pretreatment, 15% NaOH, 180W, 18kg/t NaCN	(G. Zhang et al., 2016)
Refractory gold	Alkaline Na ₂ S 2 steps: - Antimony removal with NaOH, Na₂S - Gold recovery with NaClO, NaOH	Probe type	- Antimony removal reached 94.5% under ultrasound at optimum conditions of: 60 minutes, 1M NaOH, 2M Na₂S, 1500W, 55°C (compared to 58.4% in silent conditions) - The influence of factors occurred in the order: temperature> ultrasonic power>Na₂S concentration>reaction time - Ultrasound in the step 1 allowed for the breakdown of pyrite increasing access to gold during step 2 - Gold leaching under ultrasound after maximum antimony removal improved to 68% under optimized conditions of 1.5M NaClO, 1.5M NaOH, 250W, 2 hours, 35°C (compared to 40.5% in silent conditions) - Gold leaching without antimony removal only achieved 13.35% - Ultrasound in step 2 liberated further particles trapped in pyrite	(P. Guo et al., 2019)
Refractory ore – ultrasound oxidation for	H ₂ O ₂ + KSCN	Probe type	- Sonication corrodes and damages pyrite crystal - Corrosion increases with pH, Ultrasonic power and temperature - Ultrasound increases the presence of Fe²⁺ in solution	(Gui et al., 2021a)

breaking down pyrite			- Increasing ultrasound power promotes a hydroxyl radicals and allows more oxidation of Fe^{2+} to Fe^{3+} which accelerates pyrite breakdown - Lower temperatures are preferred to prevent iron hydrolysis with an optimum of 50°C - Slightly alkaline solution preferred to prevent Fe^{2+} deposition	
Refractory gold – Gold and silver	2 steps 1. Pre-treatment with NaOH, ozone 2. Carbonized sodium cyanurate leaching	Probe type	- Ozone and ultrasound pre-treatment increased Au from 49.12% to 93.52% and Ag from 4.01% to 61.25%, reducing the time from 12 hours to 4 hours - Optimum pre-treatment conditions were: 480W, 3L/min Ozone, 0.5M NaOH and 85°C - The combination of ozone and ultrasound allowed synergistic improvement: Ozone oxidized pyrite enclosure while sonication prevented a secondary enclosure forming, and prevent agglomeration - Sonication reduced the particle size and increased the specific surface area of ore - Carbonized sodium cyanurate proved to be a better leaching agent than NaCN	(Gui et al., 2022)
Gold Concentrate – low temperatures	Barren liquor + NaCN	Probe type	- Sonication at 10°C achieved similar Au extraction to conventional leaching at 25°C (98.66% vs 98.72%) - Higher temperature resulted in increased NaCN consumption: sonication at 10°C allowed for a 16% decrease in unit consumption - At 25°C, sonication resulted in a 0.1% increase in Au recovery while reducing unit consumption of NaCN by 15% - Reaction time decreased from 24 hours to 4 hours using sonication - Sonication resulted in particle size reduction and removal of passivation films	(Yu et al., 2020)
Gold concentrate	$\text{NH}_3 + \text{Co} + \text{S}_2\text{O}_3$	Probe type	84% Au recovery achieved under optimized conditions of 0.03M Co^{2+}, 0.2M S_2O_3, 323K, 750W, 3 hours (compared to 64%) - Au recovery under sonication is 8 times faster than conventional methods - Internal diffusion appears to be the rate determining step - Activation energy decreases from 22.65 KJ/mol to 13.86 KJ/mol under ultrasound - Mechanism appears to shift towards slightly more reaction controlled as ultrasound power is increased. This is attributed to improved diffusion.	(Gui et al., 2020)
Silver processing solid waste – Ag sulfides	$\text{H}_2\text{SO}_4 - \text{NH}_2 - \text{C}_3\text{NH}_2 + \text{O}_2$	Probe type	98.6% Ag leaching achieved under: 100gpl pulp density, 7.4gpl thiourea, 28.7 gpl H_2SO_4, 24 minutes, 77°C and 80W/L	(Öncel et al., 2005)

2.2.2.3 Nickel-Cobalt-Battery metals

Due to the increasing demand for battery metals like lithium, cobalt and nickel, there has been thorough research into recycling of these elements, especially from lithium ion batteries. S.-g. Zhu et al. (2012) used H_2SO_4 and H_2O_2 with ultrasound with Lithium cobalt oxide (LiCoO) batteries from cell phones to achieve high extractions of Li and Co. Even low concentrations of H_2SO_4 in the absence of H_2O_2 , under sonication were shown to be extract more than 90% of Co. This was attributed to the generation of free radicals in aqueous solutions under ultrasound, which can form H_2O_2 . L. Li et al. (2014) compared the effects of leaching the cathode materials of LiCoO type batteries with H_2SO_4 , HNO_3 and citric acid under ultrasound. In all the acids, leaching efficiencies were increased under lower powers of 60 and 90W, while extraction at 120W was shown to be drastically lower. Citric acid was found to be the most effective leaching agent under ultrasound.

Golmohammadzadeh, Rashchi, and Vahidi (2017) also investigated LiCoO cathode material, using organic acids and ultrasound to develop a cleaner solution for leaching. Once again, citric acid demonstrated the best leaching ability. Not much improvement was observed in the leaching efficiency of lithium compared to the greater than 90% with conventional methods, but cobalt showed a 35% increase compared to conventional methods over 90 minutes of leaching. Ultrasound was shown to improve the chelating ability of citric acids. He, Sun, Song, and Yu (2015) used NMP and ultrasound to peel the aluminium foil coating from cathode materials to further concentrate LiCoO, achieving more than 99% peel off efficiency within 90 minutes. A noteworthy point was that ultrasound helped dissolve the PVDF adhesive which prevented agglomeration and increased the reactive surface area.

Jiang et al. (2018) demonstrated marked improvements in acid leaching efficiency of NMC batteries using H_2SO_4 and H_2O_2 under sonication, achieving more than 90% extraction of both lithium and cobalt in just 30 minutes. Temperature was shown to have a less pronounced effect on leaching efficiency under ultrasound, compared to conventional leaching. Interestingly, while ultrasound power was shown to positively impact leaching efficiency for both lithium and cobalt, the power at peak extraction for lithium was lower (240W) than that of cobalt. This could be due to stronger bond energies of cobalt oxides. W.-Y. Wang, Yen, and Hsu (2020) also treated NMC battery waste using H_2SO_4 and H_2O_2 to improve leaching of Li, Co and Ni while selectively leaving Mn in the residue. This was due to the precipitation of Mn, forming Mn oxides under ultrasound.

Xiao et al. (2021) used organic acids and ultrasound to dissolve both the binder and leach the battery material. Ultrasound decreased leaching time by 50% and improve the leaching percentages of Li, Co, Mn and Ni. Ultrasound was shown to increase the reaction constant of the second stage of the leaching and improve dissolution of the stable LiMnO_4 spinel structure. Z. Guo, Guo, Su, and Li (2021) used H_2SO_4 and ultrasound to extract nickel from battery sludge. Ultrasound reduced leaching time from 80 to 40 minutes. Ultrasound also had a larger impact at lower acid concentrations, due to lower viscosity and reduced energy loss in propagation, leading to more asymmetric bursting of cavitation bubbles. Power was seen to positively impact extraction.

Nivetha and Saravanathamizhan (2019) used ultrasound and H_2SO_4 to treat Ni-Cd batteries in toys and electronics achieving 98.5% extraction of nickel in 4 hours (compared to 90.8% in silent conditions), with ultrasound causing particle size reduction and more effective dissolution.

H. Li et al. (2018) treated Nickel blocks with H_2SO_4 and H_2O_2 , using ultrasound to prevent the formation of an Ni_3O_4 passivation layer. 60.41% extraction was achieved in four hours (compared to 46.29% in eight hours). Ultrasound damaged the passivation films and created many holes in the particles, which strengthened the mass transfer. The kinetics show that both systems are mainly diffusion-controlled but under sonication the system becomes more reaction controlled. Paunovic et al. (2019) improved the treatment of laterite to extract nickel, once again destroying surface films and increase the reactive surface area. The system improved from 70.32% to 91.8% Ni recovery when sonication was applied.

Marafi and Stanislaus (2011) used acids and ultrasound to leach coked oxides of hydrotreating catalysts from petroleum refining to extract Ni, Mo and V. Citric acid displayed selectivity towards Mo, V and Ni compared to sulfuric acid. Citric acid and ultrasound were shown to be the most effective (95% of all valuable metals).

Table 2.4: Battery metal sonication literature

System Studied	Reagents	Ultrasound system	Relevant notable findings	Reference
Spent Li-ion phone batteries	H ₂ SO ₄ + H ₂ O ₂	Bath type	1. Sonication at low concentrations of H₂SO₄ without H₂O₂ results in higher extraction than corresponding conditions of H₂SO₄ and H₂O₂ in the absence of ultrasound 2. Sonication at high concentrations of H₂SO₄ without H₂O₂ are less effective than corresponding conditions of H₂SO₄ and H₂O₂ in the absence of ultrasound 3. This is attributed to an improved ability to generate H₂O₂ from free radicals from water under ultrasound at low acid concentration while high acid concentrations contain less water molecules, reducing H₂O₂ formation	(S.-g. Zhu et al., 2012)
Spent LiCoO ₂ batteries	H ₂ SO ₄ +H ₂ O ₂ , HCl, Citric Acid + H ₂ O ₂	Bath type	1. 96% Co and 100% Li extraction was achieved under optimal conditions of: 0.5M Citric acid, 0.55M H₂O₂, S/L ratio 25gpl, 60°C, 5 hours, 90W ultrasonic power 2. The most effective acids were Citric>HCl>H₂SO₄ with 98.4% and 98.24% and 97.02% for Li and 96.13%, 76.42% and 45.78% for Co 3. H₂SO₄ displayed 2 steps for Co extraction where Co³⁺ is formed from LiCoO₂, and is reduced to Co²⁺ by H₂O₂ 4. HCl is a reductant and the results indicated a single step dissolution without requiring H₂O₂ 5. Citric acid was the best chelating agent but is a weak acid so ultrasound was thought to accelerate dissociation of H⁺ and improve chelation with Co²⁺ 6. Sonication powers of 60W and 90W were more effective than 120W for all acids evaluated	(L. Li et al., 2014)
Spent Li-ion batteries – active cathode material	Citric acid, DL malic acid, Oxalic acid, Acetic acid	Bath type	1. 81% Co and 92% Li extraction were achieved under optimal conditions of: 60°C, 30 gpL S/L ratio, 2M Citric acid, 1.25% vol H₂O₂, 2 hours 2. The most effective acids were in the order of Citric Acid>DL Malic>Acetic acid> Oxalic acid 3. Ultrasonic agitation significantly improved the extraction of Cobalt achieving 80% in 90 minutes compared to 55% under conventional conditions 4. Temperature was the most influential parameter 5. At temperatures lower than 45°C, Co extraction is surface reaction controlled while it becomes product layer diffusion controls at higher temperatures 6. Li extraction is product layer diffusion controlled	(Golmohammadzadeh et al., 2017)
Spent Li-ion batteries – separating cathode material from Al foil	NMP, DMAC, DMF, Ethanol, DMSO	Bath type	1. 99% peel off efficiency was achieved under optimized conditions of: 70°C, NMP, 240W ultrasonic power and 90 minutes 2. The most effective acids were in the order of NMP>DMAC>DMF>DMSO>>Ethanol 3. Sonication achieved 80% peel off efficiency for all acids except ethanol, in 30 minutes at 60°C (compared to 10% in silent conditions) 4. The mechanism is attributed to dissolution of PVDF in NMP, while sonication prevents agglomeration of particles resulting in high specific surface areas	(He et al., 2015)

Spent Li-ion batteries – active cathode material of LiCoO ₂	H ₂ SO ₄ + H ₂ O ₂	Probe type	1. 94.63% Co and 98.62% Li extraction was achieved under optimal conditions of: 2M H₂SO₄, 5% vol H₂O₂, 100 g/L S/L ratio, 360W, <30°C and 30 minutes 2. Sonication improved Li and Co extraction from 39.12 to 89.6% and 41.31 to 89.53% respectively under comparable conditions 3. 65% Co and 69% Li extraction was achieved in just 5 minutes 4. The effect of increasing the temperature from 20-30°C was significant in conventional conditions compared to the sonication tests 5. The process was diffusion controlled for both Co and Li 6. Li only required 240W of sonication power while Co required 360W – this was attributed to the larger particle size of Co	(Jiang et al., 2018)
NMC battery waste – dissolving Li metal oxide and binders	H ₂ SO ₄ + H ₂ O ₂ , H ₂ SO ₄ , H ₂ SO ₄ +Na ₂ S ₂ O ₈	Probe type	1. Leaching 2. Leaching in H₂SO₄ in the absence of ultrasound achieved >80% Li extraction and <50% of Co, Ni, Mn 3. Leaching in H₂SO₄+H₂O₂ achieved >90% for Li, Co, Mn and Ni 4. Leaching in H₂SO₄ with sonication achieved >90% Li extraction, 65-75% Ni and Co extraction and 0% Mn extraction indicating that Mn in LiMnO₂ underwent further reactions under sonication 5. The inhibition was attributed to the formation of Mn oxides under ultrasound conditions	(W.-Y. Wang et al., 2020)
NMC batteries with binder	Organic acids +H ₂ O ₂	Bath type	1. Sonication reduced leaching time by 50% and achieved almost complete extraction 2. Citric acid was more effective than Acetic acid for all metals investigated (Li, Ni, Co, Mn) except Al and Cu 3. Results for Li extraction were similar in the first 150 minutes while final results showed significant improvement due to ultrasound – attributed to binder accessible binder dissolution after which ultrasound facilitated dissolution of stable LiMnO₄ spinel structure 4. Sonication at 323K achieved 94%, 96%, 100%, 99%, 60% and 48% for Li, Mn, Co, Ni, Al and Cu under conditions of 1.5M Citric acid, 0% H₂O₂, S/L ratio 25g/L, 1440 min (compared to 89%, 89%, 87%, 91%, 48% and 83%) 5. Ultrasound was shown to suppress Cu extraction – attributed to depletion of dissolved O₂ under sonication interfering with Cu oxidation 6. The most effective conditions were: Ultrasound at 323K > Oil bath at 343K > Oil bath at 323K	(Xiao et al., 2021)
Sludge from Wastewater in battery production	H ₂ SO ₄	Probe type	1. Sonication achieved 95% Ni in extraction just 40 minutes (compared to 80 minutes under silent conditions) at conditions of: 15% mass H₂SO₄, 1:7 S/L ratio, -150µm particle size, 25°C, 600W 2. The influence of temperature is greatly decreased under sonication 3. The impact of sonication was greater at low acid concentration and solid-liquid ratios – attributed to low viscosity and decreased energy loss in propagation 4. Ultrasound power shown to improve extraction – attributed to reduced agglomeration, improved mixing and particle breakage	(Z. Guo et al., 2021)

Ni-Cd batteries	H ₂ SO ₄	Bath type	1. Ultrasound improved Nickel extraction from 90.8 to 98% 2. The impact of ultrasound was attributed to particle size reduction and improved dissolution	(Nivetha & Saravanathamizhan, 2019)
Nickel blocks	H ₂ SO ₄ +H ₂ O ₂	Probe type	1. 60.41% Ni extraction achieved under optimal conditions of 30% H₂SO₄, 10% H₂O₂, 333K, 200W and 4 hours (compared to 46.29% in 5 hours under silent conditions) 2. Ultrasound damages and peels off the Ni₃O₄ passivation layer formed, increasing the reactive surface area 3. Both methods were diffusion controlled but sonication displays more reaction-controlled kinetics than conventional methods 4. The apparent activation energy of the system decreased from 16.2 to 11.83 KJ/mol under sonication	(H. Li et al., 2018)
Laterite	H ₂ SO ₄	Bath type	1. 91.8% Nickel extraction was achieved with ultrasound leaching at conditions of 3M H₂SO₄ and 75°C (compared to 70.32% in silent conditions) 2. Sonication shown to destroy surface films and break up particles leading to increased reactive surface area and decreased diffusion layers	(Paunovic et al., 2019)
Hydrotreating catalysts from petroleum refining containing Ni, Mo, V and Al	Citric acid, H ₂ SO ₄	Bath type	1. Sonication improved extraction in all metals for both H₂SO₄ and citric acid 2. Citric acid>H₂SO₄ 3. 74.1%, 98.3%, 96.4%, 45.4% extraction achieved for Mo, V, Ni and Al in H₂SO₄ (compared to 67.9%, 88.7%, 89.2% and 37.2% in silent conditions) in conditions of: 10% H₂SO₄, 60°C, S/L ratio 1:40, 6 hours, sonicated 4. 95.7%, 84.8%, 95.7% and 18.1% extraction achieved for Mo, V, Ni and Al in Citric acid (compared to 91.5%, 83.7%, 88.2% and 19% in silent conditions) in conditions of: 10% Citric acid, 60°C, S/L ratio 1:40, 6 hours 5. Therefore, citric acid showed selectivity for Mo, V and Ni	(Marafi & Stanislaus, 2011)

2.2.2.4 Other Metals

Ultrasound has also been used in the leaching of various other metals. Tekin (2002) investigated the kinetics of dissolving calcium containing phosphate rock in HCl using ultrasound. Both the conventional system and sonicated system showed a 1st order reaction controlled leaching step with the same activation energy of 18 KJ/mol. Ultrasound increased the pre-exponential factor of the reaction due to increased collision frequencies, due to microjets and shockwaves. Şayan and Bayramoğlu (2004) improved the H₂SO₄ leaching of TiO₂ from red mud by 20% using ultrasound.

Scheelite (CaWO₄) is a common source of tungsten and is usually extracted using high temperatures, pressures under caustic or Na₂CO₃ decompositions, with passivation layers commonly formed. Z. W. Zhao, Ding, Liu, and Liang (2013) used NaOH for caustic leaching of Scheelite and found that ultrasound improved tungsten extraction. Both methods were controlled by the reaction step, but ultrasound decreased the reaction order with respect to NaOH concentration (0.8 vs 1.8 for a conventional system) in addition to increasing the pre-exponential factor. J.-h. Yang et al. (2018) further investigated scheelite treatment using Na₂CO₃, NaOH and Na₃PO₄ and found similar results for NaOH, in addition to finding that the Na₂CO₃ reaction kinetics were also reaction controlled. The apparent activation energy was unchanged at 72 KJ/mol with and without ultrasound, while the pre-exponential factor increased under ultrasound. Na₃PO₄, on the other hand was shown to be diffusion limited under conventional methods, transitioning to reaction limited under ultrasound. This difference was attributed to passivation layers of CaOH and CaCO₃ formed from NaOH and Na₂CO₃ respectively, being loose and porous, enabling the reactive surface to be easily accessible while the Ca₃PO₄ layer from NaPO₄ was dense and required ultrasound effects to renew the reactive surface area and change the rate determining step.

L. Zhang et al. (2016) sono-chemically treated roasted residue containing germanium from zinc metallurgy using HCl, CaCl₂ and various oxidising agents. Ultrasound achieved a higher extraction (92.7% vs 88.35%) and reduced treatment time from 100 minute to 40 minutes. However, after peak times were reached, the extraction was shown to decrease due to the formation of GeO₂, as the solution pH increased due to H⁺ consumption. Ultrasound also displayed a marked improvement compared to conventional methods at lower temperatures and lower initial acid concentrations, showing potential cost reductions if scaled up. Ultrasound once again was shown

to smash and erode samples and open inclusions in particles, in addition to reversing the formation of GeO_2 .

Vanadium is an important element, with 80% of the world's Vanadium being used as an additive in the iron and steel industry. Its compounds can also be used in catalysts, ceramics and batteries (Imtiaz et al., 2015). Liu, Chen, Li, and Zhao (2014) used ultrasound to improve the V extraction during NaOH treatment of a low-grade stone coal ore. These ores contain high fractions of quartz which are co-extracted with V, and therefore typically require large amounts of NaOH to process. Therefore, ultrasound was used to improve the reaction efficiency at low concentrations of NaOH. SEM displayed that ultrasound damaged the stone coal structure and improved leaching efficiencies by 12.2% compared to conventional leaching. Rahimi, Rastegar, Rahmani Chianeh, and Gu (2020) sono-chemically leached fly ash containing vanadium from thermal power plants, using organic acids and H_2O_2 . The use of organic acids was in search of a greener process than conventional methods. The fly-ash was first washed with hexane and acetone to remove the oily surface layer. The process obtained 88.7% vanadium extraction compared to 37% in the absence of ultrasound. E_h and pH measurements of the process leaching an unwashed sample with and without ultrasound, demonstrated that ultrasound accelerates removal of the oily surface layer and helped understand the impact of sonication. The E_h plummeted from 533 mV to 140 mV in 80 minutes under sonication while it dropped from 467mV to 48mV in 110 minutes in its absence. The E_h decrease was due to consumption of H_2O_2 once the oily layer was eliminated. Interestingly, the increased total E_h under sonication was attributed to production of hydroxyl radicals, which was demonstrated during measurement of E_h when treating a washed sample with ultrasound. Here, there was no variation of E_h indicating the rate of consumption matched that of production of hydroxyl radicals. Further pH analysis also yielded some interesting observation. Sonication led to lower, less fluctuating pH as the reaction progressed due to increased dissociation of H^+ from the lemon juice. This strengthens the case that sonication improves reactivity of weak acids. The lack of fluctuation was due to accelerated breakdown of the oily layer allowing consumption of H^+ to match the increased production. The pH increase during the consumption phase for unwashed samples in the absence of ultrasound was more pronounced as the oily layer consumed H^+ ions.

Chen, Bao, Zhang, and Li (2020) extracted vanadium from low grade shale rocks using H_2SO_4 and CaF_2 . The vanadium in these rocks usually exist within a strong aluminosilicate structure called

muscovite which require high temperatures and strong acid concentrations to break. Fluorides are also known to assist in breaking this structure. Therefore, ultrasound was used in conjunction with H_2SO_4 and CaF_2 to improve the current process. Sonication power was positively correlated to vanadium recovery till a plateau was reached. Low concentrations of acid showed a greater effect of ultrasound with 58% V extracted in 5% H_2SO_4 under sonication compared to just 32% under regular leaching. The difference was less pronounced under higher acid concentrations. The impact of ultrasound was attributed to breaking solid particles due to microjets, in addition to reducing the diffusion boundary layer thickness. XRD analysis shows the presence of anhydrite CaSO_4 under ultrasound while only gypsum was observed in conventional leaching. This was because ultrasound converted gypsum to anhydrite CaSO_4 , which grew and destroyed the muscovite crystal and increased the reactive surface area. SEM analysis showed conventional leaching had a dense layer of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ that wrapped around the muscovite particle, further reducing the extraction of vanadium. Sulfuric acid promoted the attack of this layer which explains why the difference in extraction between the ultrasonic-assisted treatment and conventional treatment were less pronounced at acid high concentrations. Kinetic analysis of vanadium extraction showed both processes to be diffusion controlled through the product layer with the reaction constant much higher in the sonication method. Sonication greatly accelerated the vanadium recovery, reaching a maximum of 92.93% in just 30 minutes, compared with 87.86% in 240 minutes under conventional leaching.

Indium is a scarce metal with desirable semi-conductive and optoelectronic properties. It are mainly used in LCD screens, which accounts for the majority of global indium consumption. With the increasing demand for indium and a lack of viable independent ores, recycling EOL LCD waste has been targeted. Sonication in indium extraction from LCD waste has been investigated in recent years. K. Zhang et al. (2017) used HCl to leach Indium Tin Oxide (ITO) from LCD panel without crushing in order to prevent loss of ITO present on surface of glass. Ultrasound was shown to accelerate the leaching process. Ultrasound power and resulting temperature increase in the reactor both greatly improved recovery of indium. The convective motion due to ultrasound allowed fresh contact of ITO surface with H^+ . In addition to In, sonication improved the extraction of all surface metals such as Al, Sn and Ca while Fe and Mg present inside to glass remained unimpacted,

confirming that cavitation effect acts on the surface of glass. 96.8 % recovery was obtained under optimal conditions.

Another interesting study on metal extraction was conducted by J. Kim, Kaurich, Sylvester, and Gonzalez-Martin (2006), who treated radioactive sludge from underground storage tanks. This radioactive components in the sludge can be vitrified but this can be expensive in the presence of impurities like Cr, Ca, Al, P, Mn and Fe. The chromium, in particular is present as insoluble Cr^{3+} form and therefore needs to be selectively oxidised. Therefore, applying ultrasound with NaOH and oxidants were evaluated as a potential method to remove these impurities. Interestingly, even in the absence of an oxidant, the ultrasonic assisted method managed leaching efficiencies of greater than 90% for Cr, a marked improvement from conventional leaching methods which showed 50% Cr at 80°C and 0% Cr at room temperature. It is important to note that temperatures increased from room temperature up to 80°C in the reactor due to heat transfer from the ultrasound, which is why an 80°C test in the absence of ultrasound was used as a control. Sonication assisted in the oxidation of Cr^{3+} to Cr^{4+} . Upon further analysis it was discovered that Mn recovery decreased with increasing ultrasound power and didn't show significant improvement compared to conventional extraction while Al and P improved. This suggested potential for selectivity. Fe, Al, Ca and P were all improved by sonication.

The ultrasound leaching of uranium from ores has also been investigated in recent literature. Avvaru, Roy, Chowdhury, Hareendran, and Pandit (2006) extracted U from MgF_2 tailings using HNO_3 and ultrasound. When evaluating particle sizes after treatment, there appears to be a greater particle size distribution under ultrasound. Energy input by stirring is shown to improve uranium extraction as mass transfer resistance is overcome but sonication under equivalent power shows a marked improvement compared to any stirring method. The effect of ultrasound on recovery is also more pronounced at lower acid concentrations. This is because the rate of reaction is pore diffusion mass transfer controlled in low acid concentrations, which are not sufficient to break down the MgF_2 structure. The physical effects of ultrasound allow for the breakdown of this structure and improve the pore diffusion, facilitating the reaction. The leaching of U was shown to have two leaching regimes, the first of which is the removal of uranium from MgF_2 surface, while the second stage was the removal on both the surface and the interior. Sonication enhances the first stage more than the second as cavitation effects occur on the particle surface. Furthermore, sonication allows

for a much earlier transition from the first to the second regime as microjets improve penetration and break the particle. In 0.5N acid concentration on small particles (230 microns), 85% of U was recovered under ultrasound, compared to 71% under stirring. In large particles of 420 microns, the uranium recovery improved from 62.3 to 77% in 0.5N acid under ultrasound. The paper also determined that ultrasound increases the convective diffusivity coefficient in mass transfer compared to traditional stirring. Furthermore, particle size analysis with time as the reaction proceeds indicates that both ultrasound and acid attack could both lead to particle disintegration, but the combination of both seems to be synergistic and greatly increase fragmentation.

Avvaru et al. (2008) investigated the sono-chemical extraction of uranium from a lean grade ore containing U(IV) and Fe with HNO_3 and H_2SO_4 . The U(IV) is insoluble and needs to be converted to soluble U(VI) to be leached. In the case of HNO_3 which is a strong oxidizing agent, ultrasound was shown to enhance leaching at lower concentrations of acid. At 0.88N HNO_3 , sonication improved the leaching recovery from 37 to 52.2% in 90 minutes. This was attributed to increased penetration of acid due to cavitation effects, which were not as important at high concentrations, which facilitated increased acid diffusion due to the higher concentration gradient. Furthermore, the enhancement of ultrasound due to OH radicals was thought to be negligible compared to the nitric acid concentration. In the case of sulfuric acid leaching, the Fe present in the ore reacts with sulphuric acid and can form Fe^{3+} or the complexed $\text{Fe}_2(\text{SO}_4)_3$ which could oxidize the U(IV). The extent of U leaching is dependent on the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio. An oxidant like MnO_2 can be used to improve this ratio. Ultrasound was found to enhance sulfuric acid leaching more effectively at higher acid concentrations. This was speculated to be due to formation of free radicals, H_2O_2 and H atoms which facilitated the oxidation of Fe^{2+} under acidic conditions. Ultrasound improved acid leaching using 3.75N sulfuric acid from 31.8% to 41% in the absence of MnO_2 . Furthermore, ultrasound accelerated the leaching time from 10 hours to 3.5 hours using MnO_2 and H_2SO_4 .

Table 2.5: Other metals sonication literature

System Studied	Reagents	Ultrasound system	Relevant notable findings	Reference
Phosphate rock – containing Ca	HCl	Probe type	1. Sonication was shown to increase phosphate dissolution 2. Increasing acid concentration, reaction temperature and amplitude of sonication power was shown to increase conversion 3. The reaction in both cases is shown to be chemical reaction controlled and first order with respect to H^+ 4. Both cases also have an identical activation energy of 18 KJ/mol 5. Ultrasound shown to increase rate constant by increasing preexponential factor – attributed to increased collisions of H^+ with phosphate crystal	(Tekin, 2002)
Red mud – containing TiO_2	H_2SO_4	Probe type	1. Sonication led to a 20% improvement of dissolution of TiO_2 observed compared to silent conditions 2. If maximizing TiO_2 is a priority: High yields of TiO_2 result in high yields of side products Al_2O_3 and Fe_2O_3 3. If optimizing TiO_2 with respect to selectivity, moderate TiO_2 values can be achieved with low Fe_2O_3	(Şayan & Bayramoğlu, 2004)
Scheelite – $CaWO_4$ containing tungsten, kinetics	NaOH	Bath type – with two transducers	1. Ultrasound significantly improved leaching rate 2. Both cases were surface chemical reaction controlled 3. Both cases had an activation energy of 80 KJ/mol 4. Ultrasound was shown to increase preexponential factor by increasing collision between OH^- and crystal lattice 5. Reaction order decreased from 1.3 to 0.8 using sonication indicating lower concentration dependence on NaOH	(Z. W. Zhao et al., 2013)
Scheelite – $CaWO_4$ containing tungsten, kinetics	Na_2CO_3	Bath type – with two transducers	1. Ultrasound significantly improved leaching rate 2. Both cases were surface chemical reaction controlled 3. Both cases had an activation energy of 72 KJ/mol 4. Ultrasound impact was attributed to removal of the loose $CaCO_3$ product layers	(J.-h. Yang et al., 2018)
Roasted slag containing Ge	HCl- $CaCl_2+Ca(ClO)_2$	Probe type	1. 92.7% Ge extraction achieved under optimum conditions of 80°C, 40 minutes, 3.5M HCl, 150 gpL $CaCl_2$, 58.33 gpL $Ca(ClO)_2$ and 700W (compared to 88.35% in 100 minutes under silent conditions) 2. Ultrasound shows a big improvement at lower temperatures and initial acid concentrations. 3. A low concentration of HCl with $CaCl_2$ added can increase a_{HCl} and minimize consumption while maximizing Ge extraction 4. Above 80°C, the extraction decreases – attributed to hydrolysis of $GeCl_4$ into GeO_2 5. Sonication leads to smaller particle sizes 3.46 μm (compared to 5.84μm under silent conditions) 6. Overpower occurs above 700W resulting in lower Ge extraction – attributed to decomposition of $Ca(ClO)_2$ oxidant 7. Sonication also thought to reverse GeO_2 formation	(L. Zhang et al., 2016)

Low grade vanadium ore – roasted and ground	NaOH	Bath type	1. 76.4% V extraction (compared to 64.2% under silent conditions) under optimum conditions of: S/L 1:3, 5% NaOH, 90°C, 230W ultrasound power 2. Sonicated residue was shown to be smaller than conventional residue	(Liu et al., 2014)
Fly ash from fuel oil burning – containing V	2 steps: 1. Washing with PPr 2. Lemon juice + H₂O₂	Probe type	1. 88.7% V extraction (compared to 37.5% under silent conditions) obtained under optimum conditions of: 28% lemon juice, 10% vol H₂O₂, 0.01% w/v S/L ratio, 159W, 35°C and 2 hours 2. Ultrasound shown to accelerate acid removal of oily layer in absence of PPr washing step 3. Ultrasound shown to erode particle surface 4. The kinetics under sonication show more diffusion control	(Rahimi et al., 2020)
Shale – containing Vanadium (in muscovite particles)	H ₂ SO ₄ +CaF ₂	Probe type	1. 92.93% V extraction (compared to 87.86% under silent conditions) obtained under optimum conditions of 15% H₂SO₄, 3% CaF₂, 95°C and 30 minutes 2. Reaction time reduced from 240 minutes to 30 minutes under ultrasound 3. Ultrasound shows increased impact at lower initial H₂SO₄ concentrations 4. Sonication impact attributed to increased vibration of V ions in crystal as they absorb energy 5. When CaF₂ concentration is less than 1%, silent treatment yields better V extraction – This indicates synergistic combination of CaF₂ and ultrasound in breaking aluminosilicate crystal structure 6. Anhydrite CaSO₄ formed present under sonication, compared to densely wrapped gypsum under silent conditions – Indicates ultrasound converts gypsum to anhydrite which grows as a crystals and destroys muscovite crystal	(B. Chen et al., 2020)
LCD waste – Indium Tin Oxide (ITO) – non crushing extraction	HCl	Probe type	1. 96.80% In recovery under conditions of 0.8M HCl, 300W ultrasonic power and 60 minutes 2. HCl allowed for selectivity of In over Mo during leaching 3. Significant coextraction of Al, Sn and Ca with In – these are all present on surface of ITO glass and sonication primarily acts on particle surfaces 4. Ultrasound power increased extraction of In with a peak at 300W. At greater powers Al and Mg extraction percentages increase 5. Impact of sonication attributed to rise in reactor temperature, improved convective motions promoting diffusion	(K. Zhang et al., 2017)
Radioactive sludges – containing Cr, Mn, Fe, Al, P impurities	NaOH + oxidant	Probe type	1. In the absence of an oxidant, sonication achieved a 90% Cr removal compared to 50% under conventional stirring at 80°C 0% at room temperature 2. Ultrasound facilitated oxidation of Cr²⁺ to Cr⁷⁺ 3. Al and P extraction improved as sonication power increased while Mn extraction decreased 4. Fe, Al and P extractions increase in the order: full power ultrasound> half power ultrasound> 80°C hot bath> quarter power ultrasound> shaken at room temperature 5. Mn shows little variation between methods 6. Ca extractions are better than conventional stirring at all powers evaluated	(J. Kim et al., 2006)

MgF ₂ tailings in uranium processing	HNO ₃	Bath type	1. Under equivalent power, sonication leads to improved U extraction 2. The effect of sonication is greater at low acid concentrations and smaller particles 3. The impact of sonication is attributed to particle size reduction and deagglomeration 4. Ultrasound enhances extraction of U from MgF₂ surface due to surface cavitation action 5. Particle fragmentation attributed to synergistic behaviour of acid and sonication 6. Sonication consumes less energy to achieve the same results	(Avvaru et al., 2006)
Lean grade uranium ore – U(VI)	HNO ₃ , H ₂ SO ₄ + oxidant	Bath type	1. Sonication improves U extraction in both H₂SO₄ and HNO₃ 2. With HNO₃, the leaching rate compared to silent conditions is enhanced more at lower concentrations (enhancement of 42% at 0.88N vs 8.7% at 1.76N), indicating potential of ultrasound to reduce acid consumption 3. With H₂SO₄, the enhancement rate is more at higher acid concentrations (enhancement of 5.9% in 1.87N vs 20.2% at 3.87N) 4. The mechanism of leaching with H₂SO₄ is attributed to the oxidative conversion of Fe²⁺ to Fe³⁺ under various OH radicals formed during sonication, which facilitates dissolution of U(VI). This is further amplified at high acid concentrations.	(Avvaru et al., 2008)

2.2.2.5 REEs

The use of sonication to leach Rare-earth containing minerals and media has been studied more and more intensively as the demand of REE metals increases. Tanaka, Zhang, and Saito (2002) investigated the use HCl and HNO₃ and ultrasound to extract Tb (in addition to Co and Fe) from recording media, accomplishing 100% extraction with both HCl and HNO₃. Conventional methods only resulted in 40% and 20% extraction for HNO₃ and HCl respectively. Tunsu, Ekberg, and Retegan (2014) used sulfuric acid to extract REEs from fluorescent lamp waste. Ultrasound was shown to significantly enhance Gd extraction but didn't appear to have a large impact on the other REEs.

D. Zhang et al. (2017) attempted to improve the non-oxidative acid leaching of bastnaesite using hydrochloric acid. Bastnaesite leaching is notoriously difficult as traditional methods involve oxidative roasting, converting Ce(III) to Ce(IV), which is much less leachable. Therefore, reducing agents to maintain the Ce(III), and high temperatures are required when using the oxidative roasting and leaching method. When HCl is used to treat oxidatively roasted bastnaesite, high extraction efficiencies are reached. However, Cl₂ gas is also released to the environment. Moreover, co-extraction of Th and F also occurs. Therefore, non oxidative roasting in an argon environment was proposed to prevent the oxidation of cerium, resulting in leaching of Ce(III) and other REEs. However, non-oxidative leaching with HCl in the absence of ultrasound resulted in low efficiencies. The addition of ultrasound showed greatly improved results due to the ability of ultrasound to form free radicals which act as oxidants and convert the Ce(III) to Ce(IV) which forms complexes with F⁻ and is rapidly leached, also accelerating break down of the bastnaesite and facilitating the co-extraction of other REEs. The Ce(IV) is then restored to Ce(III) by H₂O₂, instead of HCl, mitigating the release of HCl gas.

This occurs because the half equation for free radical formation is:



While that of cerium is:



So Ce(III) on the surface is oxidized to Ce(IV) due to free radicals:



Where the Ce(IV) is unstable and forms complexes with F^- and rapidly decomposes, allowing the other REEs in the ore to leach rapidly. The Ce(III) is also reformed due to instability of Ce(IV), which can get reduced by H_2O_2 . Acid mist due to chlorine gas formation is prevented due to preferential reduction of Ce(IV) by H_2O_2 .



Compared to:



Therefore, the ultrasonically assisted non-oxidative roast leach of bastnaesite was demonstrated as a safe and efficient method of REE extraction.

Rychkov et al. (2018) investigated the extraction of REEs from phospho-gypsum containing <0.45% REEs but no radionuclides. The phospho-gypsum was treated with H_2SO_4 and evaluated under grinding, ultrasonic and the use of a sorbent to absorb REE ions in solution and improve leaching equilibrium. The REEs were found to lie within the gypsum crystal, and ultrasound was speculated to breakdown this crystal and prevent aggregation and enhance the leaching. However, ultrasound alone was shown to lead to only a slight improvement (17% in conventional conditions to 23% under ultrasound) compared to a combination of these methods. Furthermore, the impact of ultrasound was only evident at sulfuric acid concentrations of greater than 10%, indicating a synergistic behaviour of the sonication and acid.

Yin et al. (2018) used MgSO_4 to extract mid-heavy REEs from weathered crust elute deposits. The REEs present on the aluminosilicates in this ore is difficult to extract due to double layers on the particles, low porosity and low active surface areas. MgSO_4 can be used preferentially to $(\text{NH}_4)_2\text{SO}_4$ to prevent ammonia pollution but usually results in low extraction efficiencies. Therefore, ultrasound was applied to the system, increasing the extraction by 53% within 11 minutes and resulting in a total extraction of 97% REEs within 30 minutes (compared to 75%

conventionally). Ultrasound increased the diffusion rate by decreasing the boundary layer thickness. It facilitated increased convective motion and enhanced the breakdown of particles due to cavitation collapse, allowing ion exchange between REE ions and Mg ions. The reaction rate under ultrasound was greatly improved in the first 5 minutes. However, the shapes of the reaction curves with time were very similar for both ultrasound and conventional methods, indicating that ultrasound affects the kinetics of the reaction. Extraction efficiency was also positively correlated to both temperature and ultrasound power. Furthermore, two stages of ultrasound extraction resulted in greater than 99% extraction of REEs.

Diehl (2018) evaluated the use of various sonication systems to improve the extraction of REEs from carbonatite rock. Usual extraction methods use large amounts and high concentrations of toxic reagents (NaOH, HNO₃) and can take long periods of time (hours). Therefore, a combination of 3% HNO₃ and 2% HCl was used in conjunction with ultrasound to achieve yields of 82% in just 15 minutes. Comparison of different sonication systems showed that probe type systems were more effective than both bath and cup-horn systems. The amplitude of frequency was also shown to be positively correlated to acoustic intensity with an optimum extraction achieved at an amplitude of 40%. Furthermore, all forms of sonication were better than conventional stirring, and even a low power ultrasound achieved better results (~63% vs ~57%). Furthermore, the low power sonication system only 1/12th of the power of the stirrer, demonstrating significant potential in energy savings using sonication.

Behera, Panda, Mandal, and Parhi (2019) treated waste scrap magnets containing ~30% Nd using acetic acid and sonication. Acetic acid, while cleaner than inorganic acids, is weak and leads to low extraction efficiencies and long reaction times. Sonication was shown to improve the dissociation of the acid in addition to breaking down the ore and increasing the surface area. The extraction increased with ultrasound power and displayed an optimum at a power of 90W, after which there was a marked decrease, possibly due to bubble coalescing. Under optimum conditions, ultrasound improved the leaching efficiency from 65.1% to 99.9% in just two hours.

Toache-Pérez et al. (2020) used PPi (tetra anion diphosphate) to selectively extract Gd and Pr from used LCD screens under ultrasound. The mechanism was attributed to the ability of ultrasound to generate H₂O₂, which could reduce Fe (III) in the feed to Fe(s), which incorporated Gd and Pr into

its crystal. This Fe(s) could be recovered using magnetic separation. 85% of the Gd and 87% of Pr was extracted. The same reaction in the absence of ultrasound does not yield any magnetic residue.

Table 2.6: REE sonication literature

System Studied	Reagents	Ultrasound system	Relevant notable findings	Reference
Recording media – containing Tb, Co and Fe	HCl, HNO ₃	Bath type	100% extraction of Tb was achieved with both HCl and HNO₃ in the presence of ultrasound at: Room temperature (increased upto 60°C due to sonication) and 1M acid - Comparatively, conventional stirring at room temperature achieved 10% and 5% Tb extraction with HNO₃ and HCl respectively - Conventional stirring at 60°C achieved 40% and 20% Tb extraction with HNO₃ and HCl respectively - Therefore ultrasound is deemed a more important factor than temperature in Tb extraction	(Tanaka et al., 2002)
Fluorescent lamp waste – containing REEs and Hg	Water, NH ₄ Cl, acetic acid, HNO ₃ , HCl	Bath type	- Water and NH₄Cl resulted in extremely poor extraction values - HCl and HNO₃ achieved better extraction values than acetic acid - Nitric acid was chosen as the best reagent due to good leaching of Eu and Y, also showing selectivity against Hg - HCl resulted in higher extractions of Hg and Gd - Ultrasound was shown to increase the extraction of Hg and Gd 95% and 97% of Eu and Y extraction occurred under optimal conditions of 0.5M HNO₃, 24h leaching time, 20°C, and a S/L ratio of 10% - Increasing temperature and leachant concentration increased Ce, Gd, La and Tb extraction	(Tunsu et al., 2014)
Bastnaesite – Ce, La-FCO ₃ , non oxidatively roasted	HCl	Bath Type	- Non-oxidative roasting in low acid concentrations and low temperatures result in low extractions of Ce and other REEs (16.43% and 16.01% in 60 minutes at 30°C, 1M HCl). This increases upto 63.87% and 62.24% at 5M HCl and 85°C. Oxy-fluorides get leached while only 4% of fluorides are leached. - Oxidative leaching in low acid concentrations and low temperatures result in low extractions of Ce (11.86%) but higher extractions of other REEs (43.74%) in 60 minutes at 30°C, 1M HCl). Good for selective separation. This increases upto 71.06% and 73.95% at 5M HCl and 85°C in just 5 minutes. Increased fluoride leach to 8%. - HCl acts as a reducing agent at high concentrations to reduce Ce(IV) to Ce(III) but results in the release of Cl₂ gas - The fast kinetics of oxidative roasting are attributed to instability of Ce(IV), which forms complexes with F and decomposes bastnaesite before being reformed to Ce(III) by Cl⁻ 65.83% and 64.86% extraction of Ce and other REEs are achieved at just 55°C, 5M in 60 minutes - The best extraction of non-oxidatively roasted ore obtained under ultrasound at high HCl and temperatures achieving 87.5% and 86.4% Ce and other REEs at 5M, 85°C and 60 minutes. Fluoride dissolution improved to 13%.	(D. Zhang et al., 2017)

			7. Sonication oxidises Ce(III) to Ce(IV) because of free radicals. These form complexes with F and break down bastnaesite rapidly, before being restored to Ce(III). 8. The formation of Cl₂ gas is prevented as the SHE of H₂O₂ is lower than that of Cl₂	
Phosphogypsum containing REEs	H ₂ SO ₄	Probe type flow cell	1. Comparison between various combinations of Ultrasound, grinding and addition of an REE dissolving sorbent 2. Leaching efficiency increases with H₂SO₄ concentration but only achieves a maximum of less than 30% due to strong bonds between REE and gypsum crystal 3. Leaching efficiency increases further when using sorbent C-160 ion exchange resin 4. Sonication alone improved recovery from 17% to 23% in higher H₂SO₄ concentrations of 30% 5. Grinding was more effective than sonication 6. Sonication showed no improvement of recovery below 10% H₂SO₄ 7. Sonication prevented aggregation of particles when combined with grinding 8. The best results were achieved with ultrasonic, grinding and a sorbent achieving >70% at concentrations of H₂SO₄ over 5%	(Rychkov et al., 2018)
Weathered crust elute deposited ore -containing REEs in aluminosilicate phase	MgSO ₄	Probe type	1. 97% total REE efficiency achieved under conditions of: 3% MgSO₄, 3:1 L/S ratio, 30 minutes, 700W compared to 75.5% under conventional conditions 2. Reaction rate due to sonication much faster than conventional in the first 5 minutes 3. At high temperatures, the enhancement of REE leaching is decreased 4. 2 stages of sonochemical leaching under optimum conditions achieves 99% REE extraction (compared to 86.2% under silent conditions) 5. Sonication decreases pyrite particle size, breaking aggregates, agglomerates and particles. It facilitates convective motions and increases contact area and time	(Yin et al., 2018)
Carbonatite rock – containing REEs	HCl+HNO ₃	Bath type, Probe type, Cup horn, varying powers	1. An optimum of 82% extraction of total REEs was achieved (compared to approximately 60% with mechanical stirring) at 70°C, 20mg/mL pulp density, 20kHz ultrasound frequency, 40% ultrasound amplitude, 3% vol HNO₃, 2% vol HCl 2. All ultrasound systems yielded better results than mechanical stirring 3. The probe setup provided the best results compared to the bath and the cup horn 4. The low frequency ultrasound bath at 25kHz and 100W achieved slightly higher REE extractions compared to mechanical stirring but only consumed 90KJ of energy compared to 1080KJ with stirring 5. The ultrasound method required a time of 15 minutes at low concentrations of reagent (<5%) and low temperatures compared to conventional methods in literature which used higher concentrations (either 7% HNO₃, or 50% NaOH), higher temperatures (upto 170°C) or longer times (upto 48 hours)	(Diehl, 2018)
Waste Scrap magnets – containing Nd	Acetic Acid, Ascorbic Acid, Citric Acid,	Bath type	1. Ultrasound assisted leaching achieved 99.9% Nd extraction in 2 hours (compared to 65.03% during conventional leaching) under conditions of 0.4M CH₃COOH, 90W, 1% S/L, 106-150 µm particles, 303K	(Behera et al., 2019)

	Formic Acid, Tartaric Acid		2. Ultrasound assisted leaching reduced reaction time to two hours compared to four hours under conventional leaching 3. Ultrasound only required 0.4M acid to achieve optimum results compared to 0.5M during conventional leaching 4. Displayed a peak at 90W of power after which it decreased at 120W 5. Residues show the emergence of pores which enhance dissolution of Nd 6. The reduction of Nd extraction as S/L ratio increased was less under ultrasound	
LCD Screen Waste – containing Gd, Fe, Pr, In, Sn, Er	PPi:H ₂ O	Probe type	1. 87% Gd and 85% Pr was recovered at conditions of 0.05M PPi, 20g/L SL ratio, 25°C, pH 6, 60 minutes, 120W ultrasound power 2. Sonication experiments generated a magnetic residue containing REEs 3. Tests without ultrasound yielded no magnetic residue 4. Tests with other reagents yielded no Gd nor Pr in either the magnetic residue nor the liquor. This showed that PPi forms complexes with Gd and Pr. 5. The magnetic residue stemmed from free radical reaction that ultimately converted Fe(III) in the sample to Fe(s) which incorporated Gd and Pr into its crystal 6. The liquor recovered Er(12%), Sn(25%) and Zn (91%) while 99%, 74% and 84% of the In, Sn and Er remained in the non magnetic residue. This showed good potential for selectivity.	(Toache-Pérez et al., 2020)

2.2.2.6 Scale-up

On an industrial scale, ultrasound assisted leaching remains rare due to a multitude of reasons. Firstly, controlled cavitation is still not a fully understood method, which poses issues during scale up (Johansson, Pamidi, Khoshkhoo, & Sandström, 2017). This could result in bubble coalescing and multiphase flow conditions that alter the various impedances of the systems and vary the required frequency and resonant power. Due to the variety of sono-chemical systems on the market, using a variety of alloy materials, reproducibility of lab scale testing can become an issue. Contradictory results can come forth due to sonication systems, experimental conditions and material studied (Abed, 2002), especially as the exact behaviour of sonication at a large scale remains largely untested.

There have been limited studies on reactor scale-up and flow cells. Xie et al. (2009) reported the industrial use of ultrasound in China to treat 5800 tons of PCB waste sludge, producing 1000 tons of 98% copper sulfate in 2007. The process was reported to be lower cost, require less energy and result in minimal waste discharge compared to traditional methods. Johansson et al. (2017) investigated the energy efficiency of cavitation for a flow cell in extracting tungsten from a scheelite (CaWO_4) concentrate. The study attempted to generate uniform cavitation, optimize the interconnected resonant systems and improve the energy efficiency in creating transient cavitation collapse.

2.2.2.7 Summary

A summary of the benefits of ultrasound leaching in literature are as follows:

1. Improved mass transfer rates
2. Faster reaction kinetics
3. De-passivating boundary layers by attacking particle surface
4. Milder reaction conditions compared to conventional controls
5. Selectivity
6. Removing the need for accelerants and other activating agents
7. Flexible, has the potential to be applied to both batch and continuous systems

However, ultrasound assisted leaching does have a few obstacles, partially due to its varied behaviour in different systems and a lack of scale-up studies. A few of the obstacles are listed below (Abed, 2002; Ensminger & Bond, 2011; Johansson et al., 2017):

1. Generation of acoustic power
2. Efficient delivery of acoustic power
3. Accurate measurement of acoustic power distribution
4. Uniform power distribution/cavitation effects. This could result in over-power of system.
The power distribution is also dependant on probe position.
5. Erosion of probe tip
6. Lack of scale up studies in literature
7. Difficulty in differentiation of physical and chemical effects

CHAPTER 3 APPROACH, GOAL AND SCOPE

As shown by the previous sections, monazite is crystalline, stable and can form passivating layers of Nd and La when leached with inorganic acids at low temperatures, leading to slow kinetics and low recoveries. While multiple methods have been studied in monazite extraction, H_2SO_4 prevails as the most common reagent for the acid treatment of monazite. However, it uses high temperatures of 200-300°C and can also be extremely time consuming (4-5 hours), resulting in high energy consumption and costs. On the other hand, ultrasound has been extensively shown to improve metal leaching, with both physical and chemical effects observed. Literature has shown it to be flexible to apply, reduce energy requirements and achieve high extractions in milder conditions. Furthermore, instead of having two steps where monazite is first converted to solid REE sulfates at high temperatures and subsequently dissolved in cold water, the act of sonication in moderate temperatures could transfer REE sulfates directly into the solution. Therefore, the application of ultrasound in sulfuric acid leaching of monazite poses an interesting question.

The methodology of this research first set out to determine one literature research objectives and two experimental objectives as follows.

Research objective:

1. Study of sonication application in metal extraction in order to determine the validity of the test and possible experimental parameters for ultrasound testing

Experimental objectives:

2. To discover sonication capability of improving direct leaching of monazite under mild/moderate conditions
3. Obtaining engineering data on the direct sono-chemical leaching of monazite using sulfuric acid

CHAPTER 4 MAIN RESEARCH: ENHANCED ULTRA-SONIC ASSISTED LEACHING FROM LOW THORIUM MONAZITE ORE BY SULFURIC ACID

4.1 Introduction

Rare-earth metals (REEs) are a group of 15 elements exhibiting similar physical and chemical properties. The recent push for sustainability has brought REEs to the forefront of research, largely due to their importance in green technology products such as wind turbines, magnets in electric vehicles and solar panels. They are also essential in electronics, superconductors, medical and nuclear technological products due to their distinct conductive, spectroscopic and magnetic properties (Balaram, 2019). Three minerals (monazite, bastnaesite and xenotime) make up 95% of the world's REE reserves. Monazite (RE_3PO_4) contains about 70% rare earth oxides, and are known to be particularly rich in valuable rare earths such as neodymium, praseodymium and samarium (B. Gupta et al., 2002). Currently, China still dominates the market in terms of REEs with 60% of current production, primarily from bastnaesite (*Mineral commodity summaries 2022*, 2022). The worldwide demand for REE supplies is steadily increasing and is expected to double in the next decade (Balaram, 2019). Monazite, in particular, could play a major role in facilitating this demand, due to its geographic abundance and coextraction with other economically viable metals (Berry et al., 2017).

The most popular method to extract REEs from monazite is wet digestion. Wet digestion in the mining industry is a hydrometallurgical process that involve using a reagent to leach materials from their corresponding source material, often in the form of ores. Wet digestion can occur at a range of temperatures and pressures (Jha et al., 2016). However, ore grade monazite is notoriously difficult to leach due to the stability of the phosphate crystal and often requires high temperatures, pressures and long times to break down (E. Kim & Osseo-Asare, 2012). The two most common methods of monazite leaching are: 1. NaOH leaching and 2. H_2SO_4 digestion followed by cold water leaching. Other leaching agents such as HNO_3 , HCl and organic acids have been investigated in literature but industrial uses for these have been sparse (Aly & Mohammed, 1999; Bandara & Senanayake, 2015; D. E. Lazo et al., 2018; Shin et al., 2012; Stone et al., 2016). The leaching reagent chosen varies with costs and availability and multiple reaction conditions have been

investigated to optimize these results. H_2SO_4 has historically been preferred to the other common inorganic acids (HCl and HNO_3) due to mitigation of toxic emissions (Cl_2 and NO_2 respectively) and the presence of the sulphate ligand which can form complexes with rare earth metals (Borrowman & Rosenbaum, 1961). The traditional sulfuric acid digestion system requires concentrated H_2SO_4 added to monazite at a dosing ratio of 1.5 and temperatures of 200-300°C for up to four hours, followed by another hour for leaching with cold water and yields recoveries of greater than 99% (Barghusen & Smutz, 1958). Due to time and energy constraints, it is evident that this method needs to be improved. Currently, studies aimed at direct leaching of monazite using sulfuric acid at milder conditions (room temperatures, low acid concentrations, short times) which have yielded REE extraction efficiencies of less than 1% (Lin et al., 2021).

Ultrasound refers to soundwaves higher than 16KHz and the application these waves has been known to significantly improve the leaching efficiencies in many processes. The effects of ultrasound have been attributed to cavitation, which occurs when bubbles are formed during negative pressures in an ultrasound cycle. These bubbles can grow and, in a process, known as transient cavitation, eventually collapse over successive cycles and result in localized high temperature (>5000K) and pressure (100 MPa) hotspots in the medium. Additionally, this collapse can generate high shear shockwaves and microjets that can attack the particle surface and increase inter-particle collision (Swamy et al., 1995). These can lead to improvements in leaching recoveries. The reasons for this improvement have been attributed to both physical and chemical effects. The physical effects are more common and are due to a combination of improved heat and mass transfer, surface activation and impact on solid-liquid interface. One of the main reasons for improvements in heterogeneous systems (such as leaching) is the formation of high velocity microjets formed during transient cavitation collapse that propagate towards particle surfaces leading to pitting and erosion, increasing the reactive surface area. Furthermore, as mentioned previously, transient cavitation results in extreme localized conditions resulting in violent collisions and high shear forces (Suslick, 2000). Chemical effects have also been reported due to the generation of free radicals created during these extreme conditions (Ameta, 2018). These radicals affect the oxidation potentials in given systems. Ultrasound has been used to improve leaching for a variety of industries like iron and copper, gold and silver, nickel-cobalt and REEs. Most studies conclude the effect of ultrasound is due to decreased agglomeration (X. Li et al., 2017;

H. L. Zhao et al., 2007), increasing access to a reactive surface by breaking down particles (He et al., 2015; Nivetha & Saravanathamizhan, 2019; Yu et al., 2020), improving the diffusion rate (Yin et al., 2018) and preventing passivation (J. Wang et al., 2020; Xie et al., 2009).

Ultrasound-assisted leaching has also been used in the REE extraction experiments (Behera et al., 2019; Tanaka et al., 2002; Toache-Pérez et al., 2020; Tunsu et al., 2014). D. Zhang et al. (2017) applied ultrasound and non-oxidative leaching to improve the leaching of lanthanides from a bastnaesite ore with HCl. The effect of ultrasound was attributed to the ability of generating free radicals that oxidise Ce^{3+} to Ce^{4+} . This forms unstable complexes with the F^- ions in bastnaesite, which further accelerates the breakdown of the ore and facilitates the co-extraction of the other REE. The Ce^{4+} is then restored to Ce^{3+} due to the presence of H_2O_2 formed by free radicals in sonication. Compared to leaching conventionally with HCl, this mitigates the release of Cl_2 gas which is formed in the absence of H_2O_2 . Then H_2O_2 gets preferentially reduced instead of HCl due to its E_h value of 0.87 (compared to 1.36 for the Cl_2/Cl^- pair). Rychkov et al. (2018) used ultrasound assisted leaching to improve REE extraction from a low grade phospho-gypsum ore with H_2SO_4 . The ultrasound improvement was attributed to breakdown of the stable phospho-gypsum crystal due to physical effects. Diehl (2018) used a mixture of 2% HCl and 3% HNO_3 to achieve an 82% extraction of REEs from carbonatite rocks in just 15 minutes, in addition to demonstrating that energy requirement lowered by a factor of 12 to comparable tests with conventional methods.

Due to the obvious benefits of sonication, in breaking down a crystal structure, increasing the reactive surface area and the proven track record of improving extraction efficiencies, the present work primarily focuses on utilising ultrasonic agitation to improve the direct leaching of monazite with H_2SO_4 .

4.2 Experimental

4.2.1 Materials, Reagents and Apparatus

The monazite ore was obtained from Congo and provided by Auxico/IGS. Due to a shortage of first batch of sample provided, a second batch, with a higher tin content was provided. The x-ray diffractions (XRD) confirm that the sample is monazite (Figure 4.1), while X-ray fluorescence

(XRF) (Table 4.1) was used to determine the quantities of elements present in the sample. The sample provided was a pulverized powder with a D₈₀ of 325 mesh.

Table 4.1: XRF analysis of monazite samples

Element	Weight Percentage(%)	
	Sample 1	Sample 2
Ce	24.218	26.656
P	6.125	5.756
Nd	13.425	14.860
Si	3.429	3.292
La	8.282	9.505
Sn	12.451	4.321
Al	1.8	0.976
Pr	2.121	2.654
Fe	5.08	2.757
Sm	1.39	1.702
Th	0.546	0.866
Y	0.471	0.565
K	0.092	0.286
Ca	0.607	0.657
Nb	0.074	0.091
Sr	0.154	0.214
Zr	0.183	0.157
S	0.044	0.159
Pb	0.041	0.054
Cl	0.151	0.149

Ta	0.093	0.136
U	0.05	0.066
Ni	0	0.052

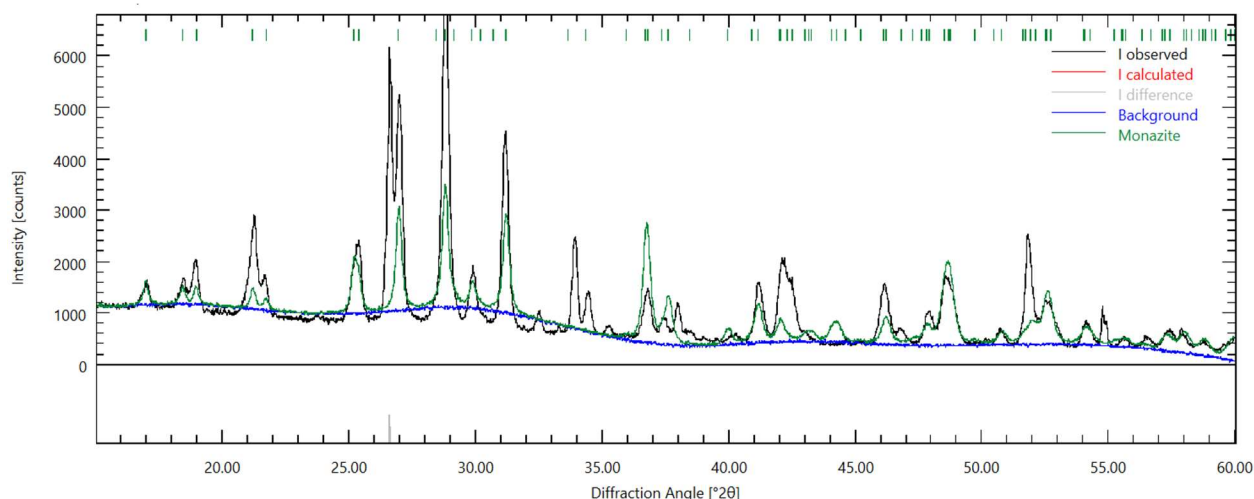


Figure 4.1: XRD patterns for monazite sample 1

The reagents used in the secondary leaching were analytical grade H_2SO_4 (50% m/v and 98% m/m), HNO_3 (70% (w/w) and HCl (37%), all obtained from Fischer™ and diluted using de-ionized water.

The experiments used a probe type ultrasound system of Synetude™ M440 ultrasonic processor with a frequency of 20KHz and a variable power input. The probe used to generate ultrasonic waves was a monel (Ni-Cu) alloy of diameter 40 mm, with a maximum amplitude of 8 μm . Sonication causes large increases (upto 80°C in our reaction vessel) in solution temperature that had to be controlled to within $\pm 2^\circ\text{C}$ using a Fischer Scientific Thermostatic ISOTEMP thermostatic water bath and a 250 mL jacketed beaker. In order to ensure a homogenous slurry, a magnetic stirrer at a constant rate of 450 RPM (optically determined to be sufficient) was used. The temperatures in the jacketed reactor were measured using a thermocouple. The scheme of the experimental set up is illustrated in Figure 4.2.

The filtration was conducted using a vacuum filter while the drying was performed in an oven.

4.3 Methods

4.3.1 Calorimetry

The calorimetric method (Contamine et al., 1995; Kimura et al., 1996) was used to calculate the power dissipation of the ultrasound system at amplitudes of 50%, 60%, 70%, 80% and 90%.

$$P_{diss} = mC_p \left(\frac{dT}{dt} \right) \quad (31)$$

Where “C_p” was the specific heat of the medium, “m” was the mass of the liquid being sonicated and (dT/dt) was the measurement of temperature with time. It is important to note that calibration was conducted with 250 mL of water.

The calibration procedure is as follows:

1. The probe is placed in a vessel of 250mL of distilled water, 3cm from the bottom of the vessel, much like the main experiments. The power delivered to the system can change with geometry and dimensions in the vessel.
2. A generator amplitude is set and the sonication is started. The temperature increase of the vessel is measured and noted with regard to time. This is done for a range of amplitudes. This experiment is repeated twice.
3. The delivered power is directly proportion to the slope of Temperature vs time.
4. The power is plotted vs each amplitude selected.

The calibration values were as follows:

Table 4.2: Calibration of ultrasound power with amplitude

Amplitude	50%	60%	70%	80%	90%
Power dissipated (W)	71	78	94	103	116

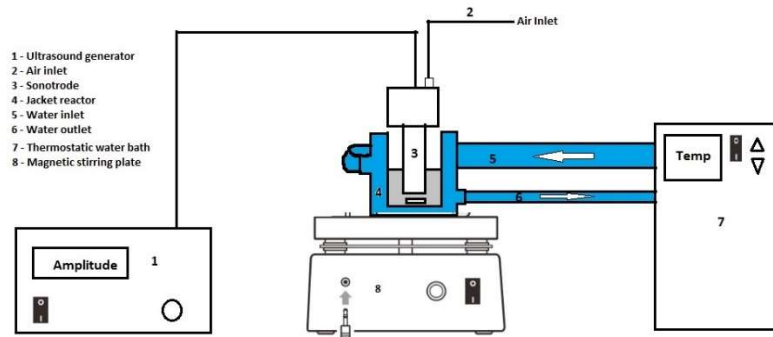


Figure 4.2: Scheme of Sonochemical leaching experimental setup

4.3.2 Leaching

The first leaching investigation directly used 8-to-15-gram samples of the 80 micron monazite. All feed samples were analysed using XRF to conduct an effective mass balance. In all experiments, the probe was positioned 3 cm from the bottom of the reactor to ensure reproducibility and homogenous mixing, without interfering with the magnetic stirrer. Initial tests showed that the probe position had an important role in extraction efficiency and the position chosen was deemed optimal. Furthermore, the temperature was maintained by running the probe and waiting for the desired temperature to be reached before adding the sample and starting the timer.

The slurry was then filtered, washed dried at 90°C for 24 hours, weighed and taken to XRF for analysis. All experiments conducted were batchwise and performed under atmospheric pressure.

$$yield = \left(\frac{m_{initial}c_{x,initial} - m_{residue}c_{x,residue}}{m_{initial}c_{x,initial}} \right) * 100 \quad (32)$$

Where “x” stands for the element in question, “ $m_{initial}$ ” and “ $m_{residue}$ ” represent the masses of the initial sample and residue respectively and “ $c_{initial}$ ” and “ $c_{residue}$ ” are the initial and final concentrations obtained from the XRF. Select samples were sent to ICP-AES to confirm the mass balance. Select samples were also sent to the scanning electron microscope (SEM) to get an idea

of morphological changes during leaching. A full walkthrough of experimental calculations can be found in Appendix A.

Due to their abundance in the sample, cerium, neodymium and lanthanum were chosen to display the REE leaching efficiencies and were reflective of the other REEs present.

In order to determine the most effective inorganic acid for direct leaching, HCl and HNO₃ under comparable acid concentrations (6M) were used to stage a single test comparison.

1. Time intervals: The first stage of the sulfuric acid leaching investigation evaluated the extraction at time intervals of 10, 30 and 60 minutes at 40% H₂SO₄, 60°C, L/S ratio of 7:1, 94W ultrasound power. The upper limit of one-hour was based on the maximum recommended usage of the sono-trode. The time investigation was also conducted without the use of ultrasound in order to demonstrate the efficacy of sonication and attempting to identify its mechanism improving the extraction efficiencies.
2. Acid concentration: The second stage of the investigation varied the acid concentration between 36% and 98 % (m/m) while maintaining the other conditions at 60°C, 7:1 LS ratio, 94W ultrasound power and 30 minutes. This was done in an attempt discern whether leaching could be effective at lower acid concentrations in order to minimize reagent costs, equipment corrosion and acid waste. Furthermore, lower acid concentrations increase the lifetime of the probe, due to decreased erosion during the leaching process.

It is important to note that despite the effectiveness of leaching at higher acid concentrations, 45% H₂SO₄ was chosen for the analysis of other trends in order maintain the lifetime of the probe and prevent variability in results as the study progressed due to unbalanced power dissipation as a result of probe erosion.

3. Ultrasound power: The third stage evaluated was ultrasound power. The ultrasound power provided to the system was varied between 78W and 116W at 60°C, 45% H₂SO₄, 7:1 LS ratio, 30 minutes.
4. Liquid-to-solid ratio: The liquid-to-solid ratio was the next stage varied during the investigation. It was varied between 3:1 and 9:1 while the other conditions were kept constant at 45% H₂SO₄, 60°C, 102W ultrasound power and 30 minutes. An additional

reason for not testing below 3:1 (and reducing potential acid consumption) was due to a combination of factors, mainly the reactor size and geometry in addition to minimum liquid levels in order to ensure probe submersion and uniformity between experiments.

5. Temperature: While literature shows a high dependence on rare-earth leaching due to temperature, this study could only vary temperature at two points between at 50°C and 60°C. The other conditions were kept constant at 45% H₂SO₄, 7:1 LS, 102 amplitude, 30 minutes. This was because the maximum recommended safe usage temperature of the Synetude™ system for a prolonged period was 60°C while temperatures lower than 50°C proved impossible with the water-bath system used due to the rapid temperature increases from the higher power ultrasound in the small reaction vessel. Therefore, the parameter could not be varied without changing the system configuration and ultimately affecting the reproducibility.

The optimal conditions were also evaluated under silent conditions to determine the total improvement of ultrasound while SEM analysis was used to analyse these results.

The experiments were also repeated twice and the XRF results were also analysed twice. The mean of all these results was used for all graphical displays while the standard deviation was calculated using the standard deviation and variance functions on excel. A total of 48 tests were conducted for these results, while an additional 20 were conducted for preliminary testing.

In order to maximize extraction, a two-stage leaching was also conducted once optimal conditions were determined. The filtered and washed leaching residue from the first stage was once again placed in identical conditions to the first leaching stage.

4.4 Results and Discussion

4.4.1 Acid Comparison

As displayed on Figure 4.3, both HCl and H₂SO₄ display similar levels of REE extraction with little variability between repeat runs. However, HNO₃ showed large variability which was as a result of the noticeable erosion of the probe during tests under HNO₃. Meanwhile, both HCl and HNO₃ can be corrosive to process equipment and have a high relative volatility, emitting Cl₂, HCl

and NO₂ gases (Souada et al., 2018). Furthermore, HCl didn't show great improvement over H₂SO₄. Therefore, H₂SO₄ was affirmed as the best acid for subsequent testing.

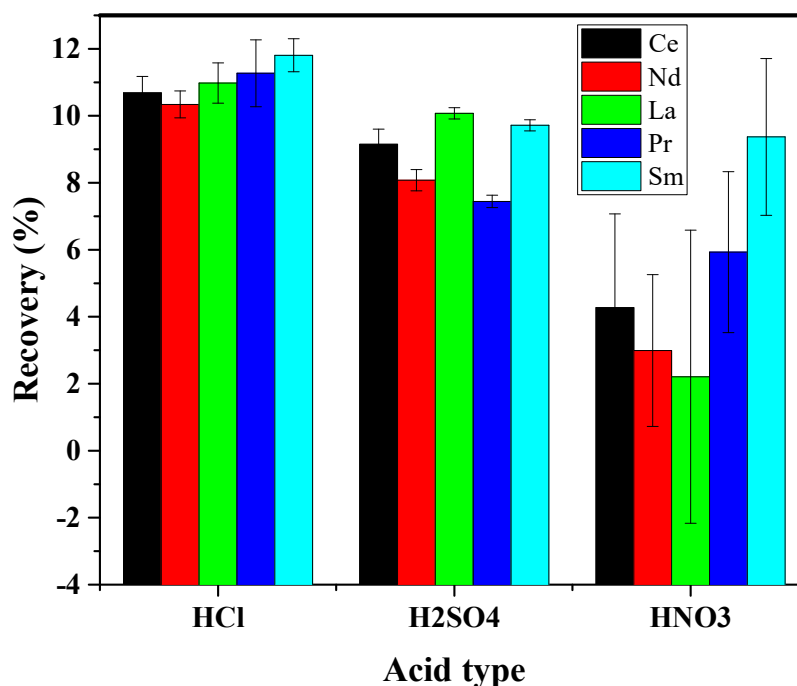
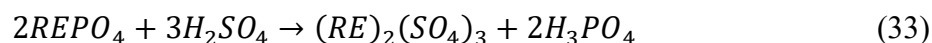


Figure 4.3: Comparison of reagent type at conditions of 6M reagent, 94W, 60°C, 7:1 L/S ratio and 30 minutes

4.4.2 Sulfuric Acid Leaching



As the experiments are conducted in low temperatures (compared to conventional digestion methods), the recoveries observed are attributed to the production of soluble rare earth sulphates and complexes shown in equation 33. The recoveries yielded consistent results in both sets of experiments.

4.4.2.1 The effect of Time

The different kinetics seen in Figure 4.4 could signify that the mechanism under sonication could be different to that without ultrasound. It shows that the effect of ultrasound is immediate achieving 8.49%, 6.97% and 8.76% for cerium, neodymium and lanthanum respectively, indicating rapid breakdown of the monazite, potentially amorphizing the crystal. The reason for believing the crystal might be amorphized is because the effects of ultrasound are mechanochemical, and crystalline monazite is more stable under sulfuric acid than non-crystalline phases (E. Kim & Osseo-Assare, 2012). Furthermore, increasing the reactive surface area can facilitate increased leaching at the particle surface, where cavitation effects directly act, both consistent with literature (B. Chen et al., 2020; E. Kim & Osseo-Assare, 2012). The slow increase in recovery between 10 and 30 minutes indicate a different mechanism, which could be associated with the reaction progressing with normal kinetics, with acid attack breaking down the internal structure of monazite and enhancing the reaction due to normal shrinking core leaching kinetics. The extraction appears to plateau at 30 minutes, which could indicate an optimum value for the system. However, solubility constraints for the rare earth sulphates should also be noted as a factor (E. Kim & Osseo-Assare, 2012; Lokshin, Tareeva, Ivlev, & Levin, 2005).

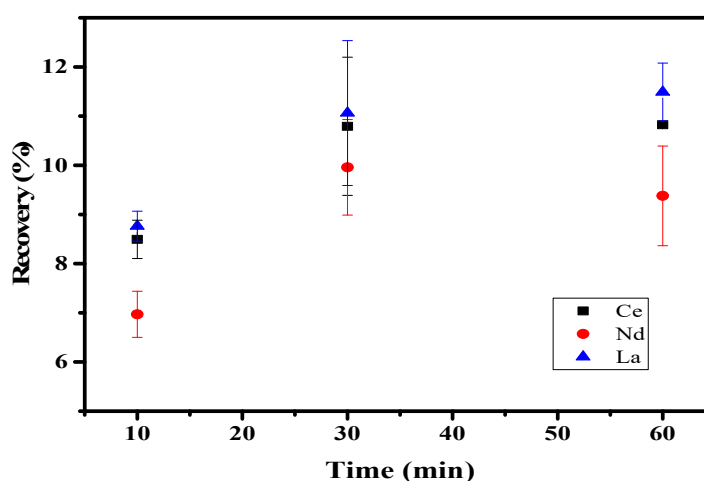


Figure 4.4: Recovery with respect to time at 40% H_2SO_4 , 7:1 L/S Ratio, 60°C and 94W

4.4.2.2 The effect of Acid concentration

The results displayed in Figure 4.5 show that increasing acid concentration improves the leaching efficiency. This trend is very common in literature and could be attributed to the increased availability of acid, allowing increased diffusion to attack the particle surface, thereby increasing the extraction (Z. Guo et al., 2021; Liu et al., 2014; Rychkov et al., 2018; Yin et al., 2018).

Figure 4.6 compares conventional leaching with sonication under 98% acid concentration and clearly demonstrates that sonication achieved at least a 33% improvement for all REEs evaluated. This can once again be attributed to aforementioned advantages of sono-chemical leaching. The improvement at high concentrations is far lower than at low concentrations and possible theories will be explained later. The optimum chosen concentration of sulfuric acid is 98%.

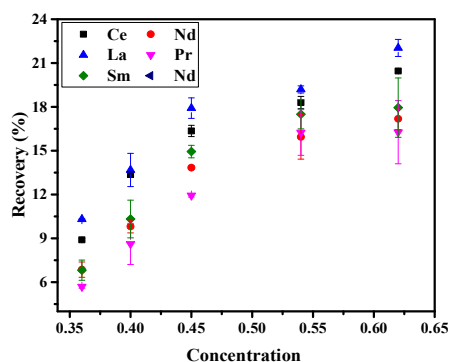


Figure 4.5: Recovery with respect to acid concentration at 7:1 L/S Ratio, 60°C, 94W and 30 minutes

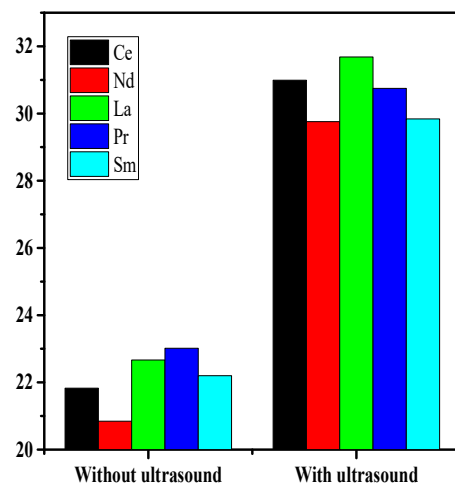


Figure 4.6: Comparison between sonicated and conventional treatment at 98% H_2SO_4 , 7:1 L/S ratio, 60°C, 94W and 30 minutes

4.4.2.3 The effect of Ultrasound Power

It is interesting to note that recoveries fluctuates from 73-102W but there appears to be a clear optimum at 102W (Figure 4.7). Increasing the ultrasound power is known to increase the number and size of bubbles during cavitation (Meroni et al., 2022), and therefore increase the cavitation effects during leaching. Studies have shown that this has indeed increased leaching efficiencies (Fu et al., 2017; Turan et al., 2019; W.-Y. Wang et al., 2020; G. Zhang et al., 2016; K. Zhang et al., 2017). The decrease in leaching efficiencies at 116W is attributed to the formation of bubble clouds which coalesce at higher powers which results in shielding effects. Furthermore, increased bubbles are known to decrease the energy transfer from ultrasound. This effect has also been seen in literature (Behera et al., 2019; Fu et al., 2017; H. Li et al., 2018; L. Li et al., 2014). This effect can be confirmed by Figure 4.8, which shows SEM images of particles at 102W of sonication are smaller and more porous compared to 116W, which also appear to display pitting, but are generally larger and smoother. Therefore, an optimum of 102W was chosen.

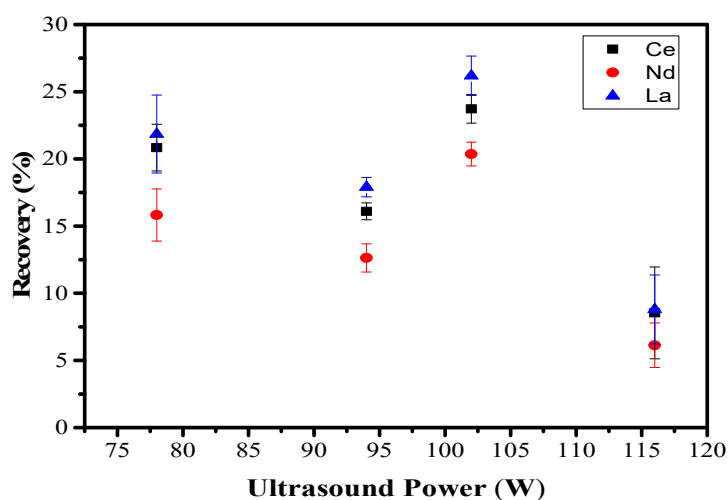


Figure 4.7: Recovery with respect to ultrasound power at 45% H_2SO_4 , 7:1 L/S Ratio, 60°C and 30 minutes

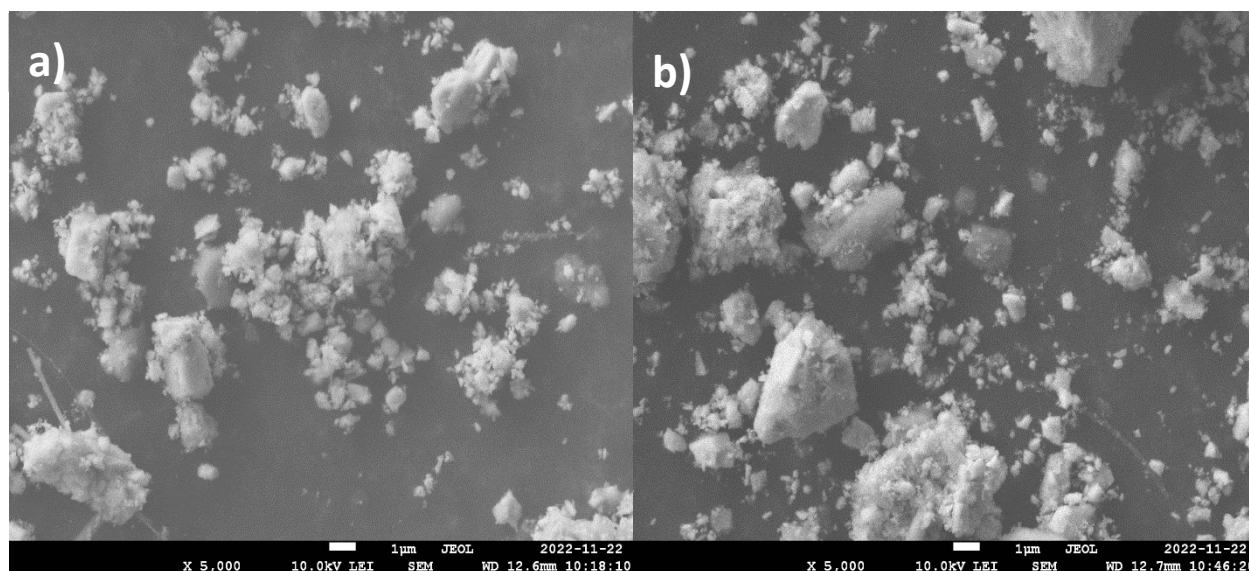


Figure 4.8: a) Monazite residue after 102W sonication, b) Monazite residue after 116W of sonication

4.4.2.4 The effect of Liquid-Solid Ratio

The recovery for all rare-earths observed increases with the liquid-solid ratio as shown in Figure 4.9. This is consistent with leaching literature and is thought to be due to increased availability of leachant and less diffusion resistance for surface contact with the particle (Rahimi et al., 2020). Further solubility can also be facilitated due to crowding of more soluble elements such as iron (Behera et al., 2019). Furthermore, cavitation becomes more difficult under higher viscosity and therefore sonication under higher liquid to solid ratios are known to increase recovery during leaching (Jiang et al., 2018). The optimum is chosen at a ratio of 7:1.

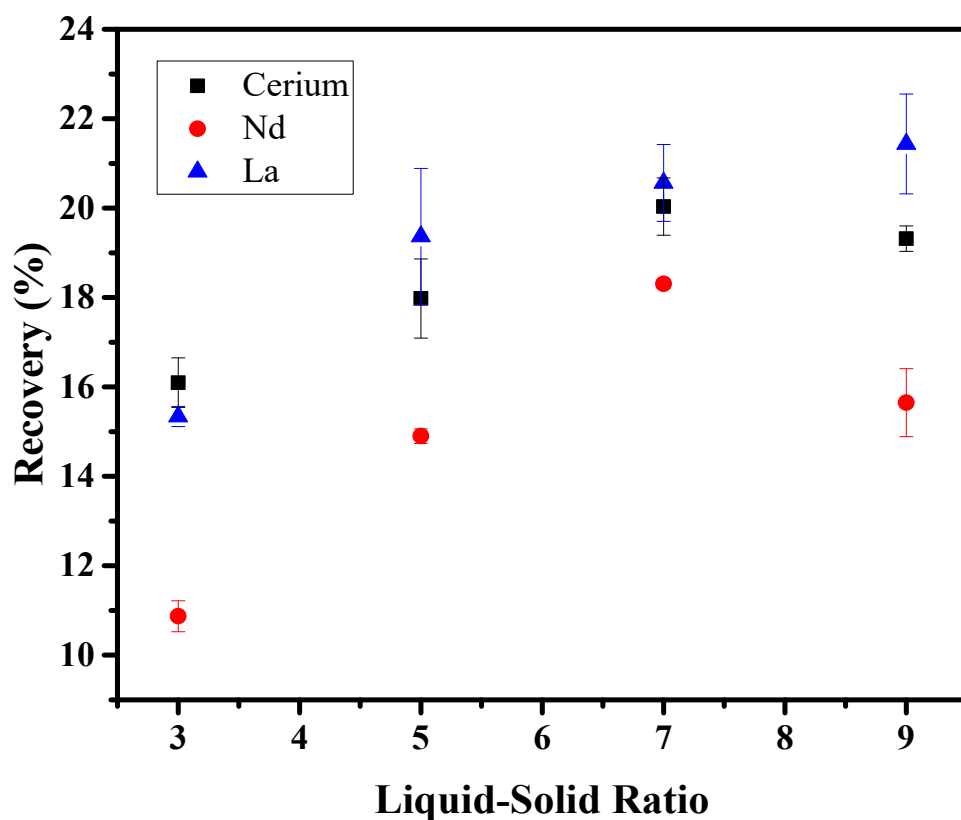


Figure 4.9: Recovery with respect to L/S ratio at 45% H_2SO_4 , 60°C, 102W and 30 minutes

4.4.2.5 The effect of Temperature

Despite the limited range, the temperature is clearly proportional to the recovery (Figure 4.10). This can be explained with basic thermodynamics as higher temperatures lead to an increased collisions and number of particles with the necessary activation energy to break the monazite crystal structure and release REEs for leaching to proceed.

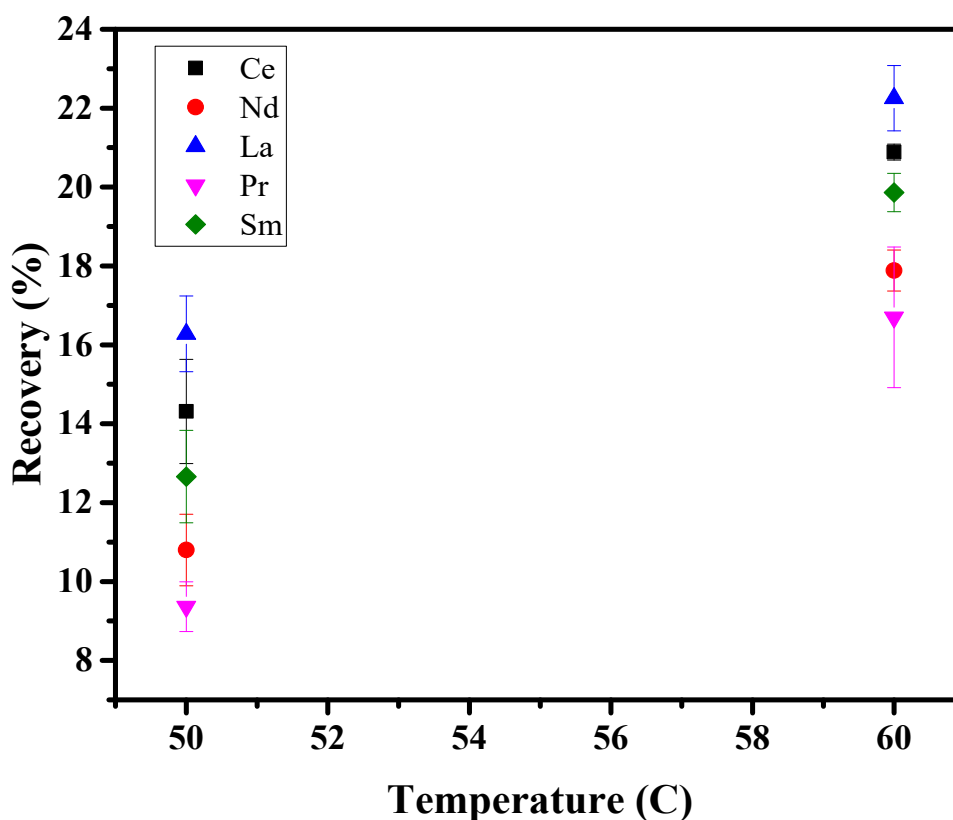


Figure 4.10: Recovery with respect to temperature at 45% H_2SO_4 , 7:1 L/S Ratio, 102W and 30 minutes

4.4.2.6 Comparison with Conventional Leaching

The results for silent treatment is in accordance with literature (Lin et al., 2021) (slightly higher on account of higher acid concentration) and confirms gradual leaching of monazite with slow reaction kinetics reaching 1.5%, 0.85% and 3.02% in an hour (Figure 4.4) for cerium, neodymium and lanthanum respectively. As mentioned previously, Ultrasound-assisted leaching, by comparison shows an immediate jump in leaching efficiency within just 10 minutes, followed by a slight increase from 10 to 30 minutes. Therefore, it is safe to assume that the effect associated with ultrasound acts within the first 10 minutes and can be attributed to rapid breakdown of the monazite and possible amorphization of the crystal due to mechanical effects of microjets. There is also an

increase in reactive surface area, due to surface cavitation effects, which improves leaching recovery.

These advantages are evident in the SEM analysis shown in Figure 4.11, where particles undergoing conventional leaching are larger and smoother than those under sonication, which are comparatively smaller and display heavy pitting, indicating the effect of breakdown due to microjet. This further supports literature that sonication increases the reactive surface area for surface acid attack. The Tru-Q elemental analysis in Figure 4.12 and Figure 4.13 also shows that very little breakdown of monazite occurs under conventional leaching, while sono-chemical leaching yields a higher fraction of small particles (most at 1.42 microns, diameter) containing less than 5% cerium, neodymium and lanthanum.

As shown in Table 4.3, the improvements due to sonication are more drastic at lower acid concentrations. One potential reason is that conventional leaching at high concentration facilitate monazite crystal breakdown due to acid attack, while sonication already breaks down these large particles, even at low concentrations. Another consideration is that high acid concentration leads to higher solution higher viscosity, which can reduce the cavitation effects and reduce the impact of sonication.

The low overall leaching percentages (less than 40%) even under sonication could be attributed to strong bond energies in the monazite crystals preventing total liberation of REEs from the monazite crystal at the low temperature temperatures evaluated, despite the auxiliary energy provided by sonication.

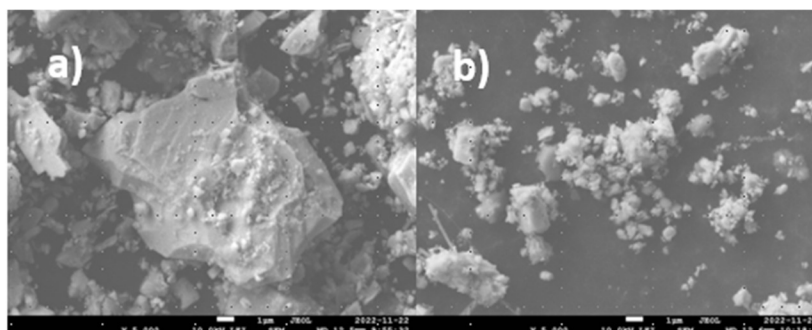


Figure 4.11: a) Monazite residue after conventional leaching at 40% H₂SO₄, 60°C, LS: 7:1 and 30 minutes b) Monazite residue under 102W sonication at 40% H₂SO₄, 60°C, LS: 7:1 and 30 minutes

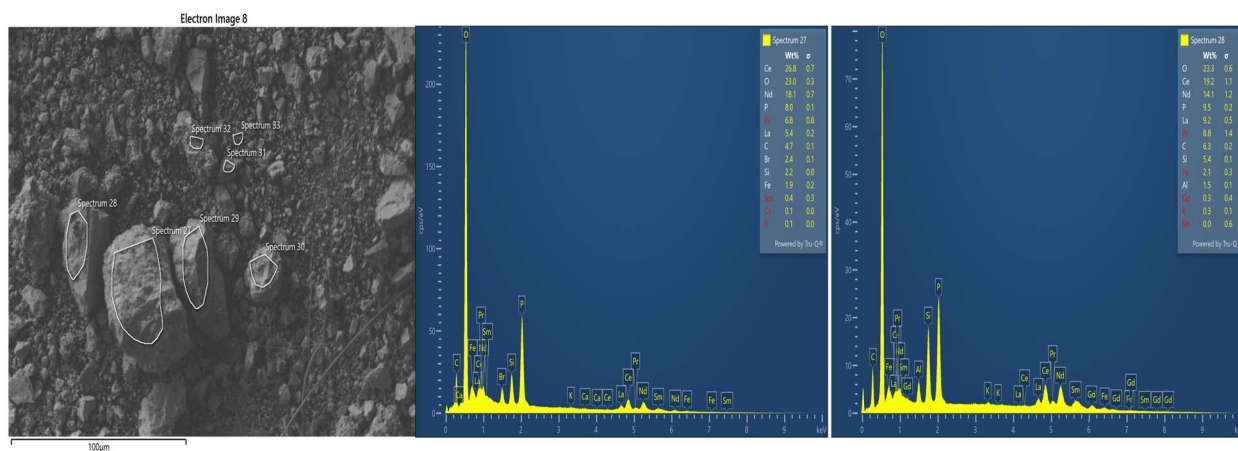


Figure 4.12: TRU-Q elemental analysis of conventional leaching of monazite

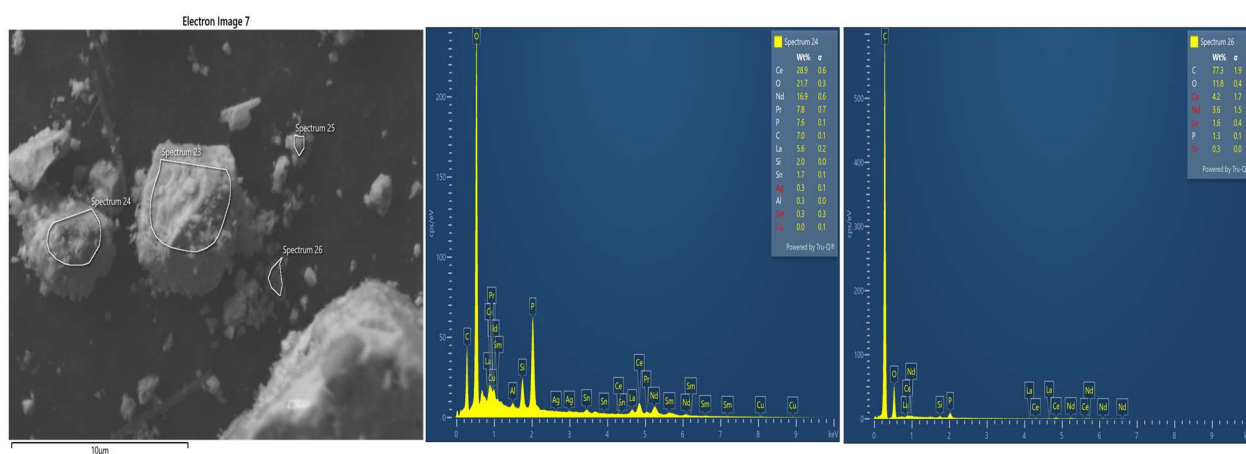


Figure 4.13: TRUE-Q elemental analysis of sono-chemical leaching of monazite

Table 4.3: Percentage improvement of sonication compared to conventional leaching

	Percentage improvement between conventional and sonication	
	40% H ₂ SO ₄	98% H ₂ SO ₄
Cerium	604	42
Neodymium	1070	43
Lanthanum	924	40
Praseodymium	829	34
Samarium	760	34

4.4.3 Two-stage leaching

The maximum REE extraction observed during two-stages of leaching does not exceed 45% as shown in Figure 4.14. Comparatively, the classic digestion method achieves more than 90% extraction of REEs from monazite (Jha et al., 2016) using a less than a third of optimum sulfuric acid dosing in this study. However, these methods also utilize temperatures between 200 and 300°C for periods of two to four hours, indicating that the sonication method could result in large time and energy savings upon further improvement.

The temperature constraints of this sono-trode prevented more detailed analysis of the process but the results from the temperature trends indicate that this study could be further improved by employing sonication at higher temperatures. Moreover, NaOH treatment of monazite requires lower temperatures (120-140°C) (Jha et al., 2016) than acid digestion, so using these methods to employ sonication for NaOH digestion could also yield interesting results. However, these results indicate that sonication in these conditions is insufficient to completely breakdown the phosphate crystal in monazite. Therefore, further studies to study ultrasonic assisted acid leaching of dephosphorized monazite could yield interesting results in the field of REE extraction.

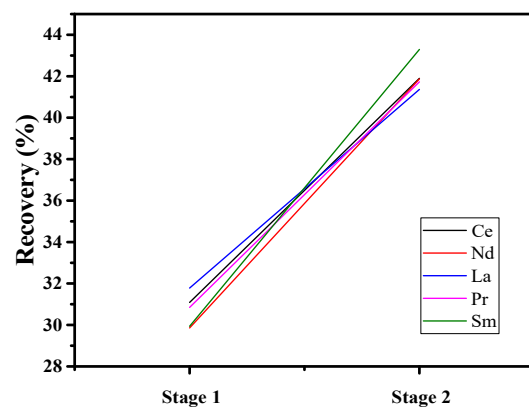


Figure 4.14: Two-stage, optimal conditions of 98% H_2SO_4 , 9:1 L/S ratio, 60°C, 102W and 30 minutes

CHAPTER 5 DISCUSSION AND ADDITIONAL RESEARCH

5.1 Probe Position and Reactor geometry

Early in the research, there were some interesting points of note that resulted in methodological updates. Early testing indicated very uneven results between runs and was the source of a lot of confusion. It was only then, that tests were conducted at different levels of probe immersion and reactor geometries. The results showed that both factors were crucial to repeatability of experiments. In fact, almost no REE extraction improvement occurred when the probe was placed too high. Maximum probe immersion and wider reactor geometry delivered better extraction results. This was then corroborated with research and occurred due to:

1. Wider reactor geometry: Improved results as a result of increased contact area between reagent and ore in addition to a more homogeneous distribution of particles in the ultrasound field.
2. Improved immersion: In heterogenous S-L mixtures, low probe immersion ensured homogenous propagation of ultrasound field and homogeneous mixing
3. Unpredictability of ultrasound mechanism

Therefore, the probe position and reactor type were standardized for the duration of the investigation. This was a brief investigation and was only provided an insight into sonochemical mixing behaviour. The results shown in Appendix B, display higher recovery values than those in chapter 4.4 but these tests were conducted on an older monazite sample, with possibly less crystalline $\text{RE}(\text{PO}_4)$, and so should be taken independently than the research in 4.4. Results of sample testing could be found in Appendix B.

These results indicate that reactor and sonotrode designs need to be further improved for any possibility of scale up and widespread adoption in industry. Efforts are already made as described in section 2.2.1.3 and Ensminger and Bond (2011).

5.2 De-phosphorized Monazite Testing

Based on section 2.1.2.3, leaching of pretreated monazite has been routinely investigated in literature. The act of pre-treating monazite is to break the energy intensive phosphate bond. Once

this bond is broken, leaching the REEs from the solid phase into becomes much easier and has been routinely conducted. The results in 3, led to further investigation on the leaching of de-phosphorized monazite using HNO_3 . However, the experimental results were not put forth in this investigation as they are still in progress and deemed outside the scope of this research. It is interesting to note, however, that they are showing promising results achieving satisfactory results at lower acid concentration and shorter times than conventional methods. Furthermore, inhibition of U and Th into the leaching solution has also been observed.

5.3 Building an Inline system

Another interesting piece of work that was conducted over the duration of the research was the building and cold commissioning of an inline sono-chemical reactor designed to process 5L/hour of laterite slurry. This project was conducted in collaboration with Canadian American Nickel (CAN) and Impact Global Solutions (IGS). The project was designed to be the first step in one of the first industrial sono-chemical leaching projects of its kind. The sonochemical reactor was a UIP400hdT from Hielscher and the system was designed to treat Laterite ores. The Process Flow Diagram is illustrated in Figure 5.1.

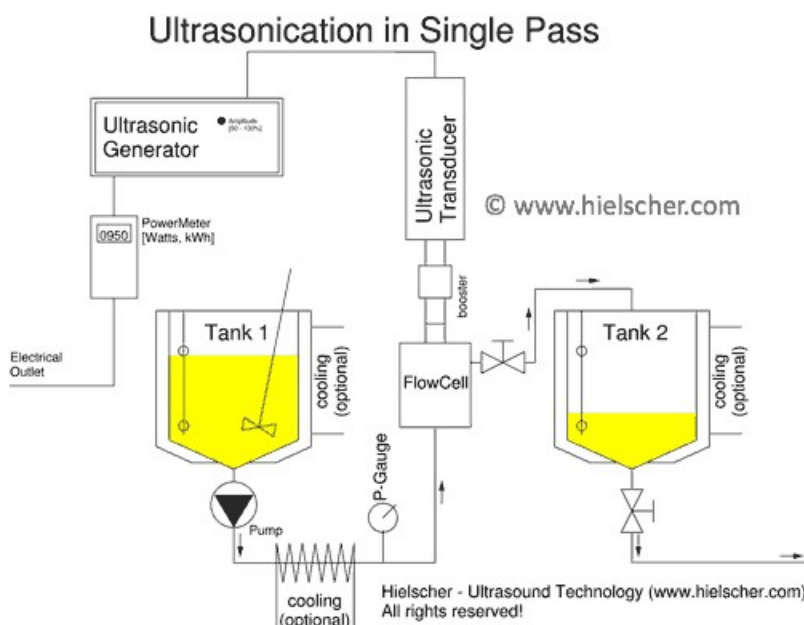


Figure 5.1: PFD of pilot inline sonication system

The reactor was assembled and tested as shown on Figure 5.2.



Figure 5.2: Assembled pilot plant

The IGS team first ran experiments at a batch scale with a probe time Hielscher probe in order to determine whether sonication works to improve laterite leaching. The actual testing values are confidential and so the figures in Table 5.1 below are a representation of the actual results. This example is displayed in order to form a basis for scale up values. The testing resulted in acceptable results at the conditions similar to that of Table 5.1.

Table 5.1: Ultrasound parameters/results for IGS batch testing

Volume (mL)	133
Sonation time (minutes)	60
Probe Power (W/cm²)	10.52
Probe area (cm²)	3.8
Energy Delivered (Ws)	144,014
Energy delivered per unit volume (Ws/mL)	1082

The energy delivered value was measured from the reading on the generator. The Energy delivered per unit volume was calculated by:

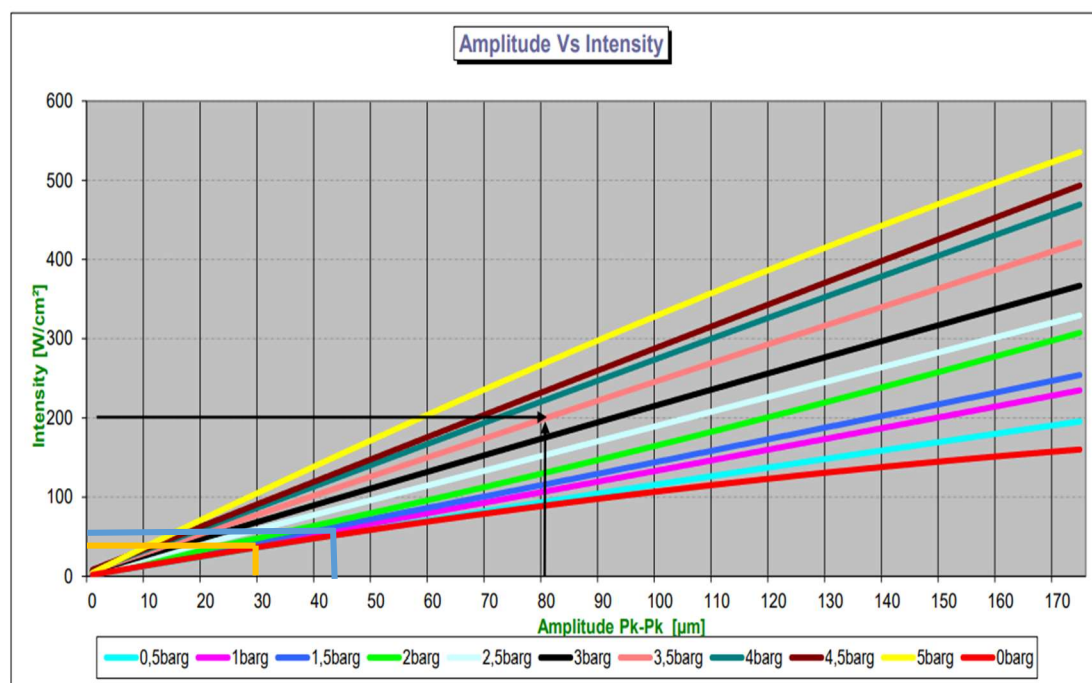
$$\text{Energy Delivered per unit volume} = \frac{\text{Energy Delivered (Ws)}}{\text{Volume of slurry (mL)}} = \frac{144,014}{133} = 1082 \text{ Ws/mL} \quad (34)$$

This value and the total energy delivered values were important in setting the benchmark for the inline system and was used to select an appropriate probe from Hielscher.

The Hielscher probe chosen was UIP400hdT and was designed to provide ultrasound intensity values within the range of values obtained from batch testing. The goal is to optimize the leaching extraction results while minimizing the energy consumption. Hielscher probes are designed to provide flexibility to their intensity values by inserting an adjustable booster or reducer to adjust the maximum amplitudes.

UIP500hdT - UIP4000hdT Sonotrode	Frontal area [cm²]	Max. Amplitude*(Pk-Pk) at 100% [µm]									
		Booster as Reducer						Booster as Booster			
		B4-2.2	B4-1.8	B4-1.4	B4-1.2	No Booster	B4-1.2	B4-1.4	B4-1.8	B4-2.2	
For UIP500hdT – UIP2000hdT (amplitude at the horn 25µm):											
BS4d18	2,5	39	47	61	70	85	102	119	153	187	
BS4d22	3,8	26	32	41	47	57	69	80	102	125	
BS4d22L2	4,5	45	55	72	83	100	120	140	180	220	
BS4d34	9,0	11	13	17	20	24	29	34	43	53	
BS4d40	12,5	8	9	12	14	17	20	24	31	37	
BS4d50	19,6	11	14	18	21	25	30	35	45	55	
CS4d40L1	17	14	17	21	25	30	36	42	54	66	
CS4d40L2	25	16	19	25	29	35	42	49	63	77	
CS4d40L3	33	16	19	25	29	35	42	49	63	77	
CS4d40L4	41	16	19	25	29	35	42	49	63	77	
RS4d40L3 axial	13,4	10	12	16	18	22	26	30	40	48	
RS4d40L3 radially emitting	276	2	3	3,5	4	5	6	7	9	11	
RS4d40L4 axial	13,4	10	12	16	18	22	26	30	40	48	
RS4d40L4 radially emitting	420	2	3	3,5	4	5	6	7	9	11	

Figure 5.3: Maximum amplitude values for Hielscher sonotrodes



Example:

Figure 5.4: Intensity vs amplitude curves at different Pressures

Figure 5.3 and Figure 5.4 are from the device manual for Hielscher sono-trode, the Hielscher UIP400hdT. Figure 5.3 denotes the maximum amplitude for various probes without an adjustable booster/reducer, with a booster and with a reducer. These amplitude values on the table were experimentally determined in water at RTP. The value highlighted in Figure 5.3 was the maximum amplitude for the probe and booster purchased by IGS.

Figure 5.4 is a graph of maximum intensity at various pressures and amplitudes. These values are also determined with water at RTP. The amplitude obtained from Figure 5.3 could then be used in Figure 5.4 to determine the intensity of the probe booster/reducer system. It is important to note that these values could also be reduced by adjusting the % amplitude of the system.

While these values are utilized for the manual calculation, the UIP400hdT contains real time data on delivered energy in the actual slurry medium and can be used for much more accurate calculations. However, this tabular method can be used for equipment selection calculations.

The energy consumption values from the batch experiments are used as the benchmark for testing the continuous system. The surface intensity for a CSd40L1 probe with a booster had an amplitude

of 42 microns. At a system pressure of 1 barg, this translates to $60\text{W}/\text{cm}^2$ and can be read from Figure 5.4. The probe area is 17cm^2 and therefore this translates to a power of 1020W provided by the probe. From equation 31, it is clear that $1082\text{Ws}/\text{mL}$ is required in order to sufficiently sonicate the laterite.

$$\frac{1}{1082} \frac{\text{mL}}{\text{Ws}} * 1020\text{W} * \frac{1\text{L}}{1000\text{mL}} * 3600 \left(\frac{\text{s}}{\text{hr}} \right) = 3.39\text{L/hr} \quad (35)$$

This was the baseline flowrate for the inline testing. From here, the flow-rate could be increased in order to determine if the leaching is still successful. After this, both the amplitude and pressure could also be varied in order to determine the optimal parameters with regard to total energy consumption of the system.

Another point to note is that due to differences in manufacturer, if the supplied energy values for batch testing are determined using a different probe, it is important to calculate the dissipated energy values in the experiment using calorimetric methods ((Kimura et al., 1996) and then recalculate for the new system, adjusting for a different set of inefficiencies for the manufacturer of the inline probe.

Once the reactor was functional and went through cold commissioning, the rest of the study was conducted by IGS and outside the scope of this research.

CHAPTER 6 GENERAL DISCUSSION

The investigation provided a great deal of clarity about the utilisation of ultrasound to enhance leaching. Firstly, the thorough literature review of monazite in 2.1 put forth the current issues in monazite treatment and provided a background to all the methods used. Section 2.2 introduced sonication and delved into its usefulness in leaching metals from various ores. This suggested that ultrasound could indeed be used as a greener method of monazite leaching which was covered in the 3 and suggested that it did improve direct leaching of monazite, but not to the extent that was to be expected. The additional research described in 5.1 confirmed that probe position and reactor geometry were vital in achieving higher values of extraction and raised salient questions about scaleup possibilities and reactor design. Section 5.3, describing the development of an inline pilot project for REE extraction demonstrated possible steps in scale up and conversion from batch to continuous testing, especially with regard to optimization of ultrasound energy.

CHAPTER 7 CONCLUSION AND RECOMMENDATIONS

7.1 Conclusions

The experimental research objectives of:

1. To discover sonication capability of improving direct leaching of monazite under mild/moderate conditions
2. Obtaining engineering data on the direct sono-chemical leaching of monazite using sulfuric acid

Conclusion and discoveries:

1. The research demonstrates that ultrasonic-assisted leaching yields improved the treatment compared to the silent leaching. Under optimum conditions of 98% H_2SO_4 , 102W ultrasound power, 60°C, 7:1 LS ratio and 30 minutes reaction time, which resulted in 31.9%, 30.7% and 32.8% for cerium, neodymium and lanthanum respectively. This was compared to 21.8%, 20.8% and 22.7% respectively under silent conditions. The result improved to 41% for all REEs upon two stages of sono-chemical leaching.

2. With the monel alloy probe used, both HCl and H₂SO₄ display similar leaching efficiencies, while HNO₃ has much more variable results, potentially due to probe erosion during the experiment, which interferes with leaching.
3. The reaction mechanism under sonication appears to be different in comparison to the silent conditions for all REEs evaluated. Under sonication, more than 7% of all REEs were extracted in just 10 minutes compared to less than 3% in an hour in silent conditions. The silent leaching displays slow kinetics with gradual increase from 0.3 to 3% over the 60 minutes. However, sonication appears to exhibit two stages of leaching. The first stage appears is attributed to the surface effects of ultrasound which rapidly occur within 10 minutes, reaching 8.49%, 6.97% and 8.76% extraction for cerium, neodymium and lanthanum respectively. This is followed by a slow, gradual increase to 10.79%, 9.95% and 11.06% which could be associated with shrinking core reaction kinetics.
4. SEM analyses show that sonicated particles are smaller and more porous than those undergoing conventional leaching, indicating that ultrasound is effective at breaking down the monazite crystal structure, increasing the reactive surface area and preventing aggregation.
5. In summation, ultrasound is a powerful technique to enhance the recovery of REEs from monazite, but the technique still requires significant expansion of investigation and improvement in order to be used in industry

Our additional research in section 5.1 also had an interesting conclusion with regard to possible use of this method on an industrial scale. The variability of results based on probe position and reactor geometry indicated a potential obstacle in scaleup. In conclusion, while sonication yielded an improvement over direct, silent leaching of monazite, the study used at least three times the amount of H₂SO₄ in comparison to conventional industrial methods. However, the experiments are conducted at significantly lower temperatures (60°C) for shorter times (30 minutes) which shows potential in alleviating cost and energy requirements.

7.2 Future Studies

Therefore, this study requires further expansion by using probes that can handle moderate temperatures (80-90°C) and further improvement in sonication technology in order to make this

process industrially and economically viable. The application of sonication to the NaOH treatment of monazite or to treat de-phosphorized monazite, also shows great potential for future research. The NaOH treatment method, in particular, currently uses temperatures of 120°C for 2-4 hours to achieve greater than 98% REE recoveries. Based on our results to improve sulfuric acid leaching, which generally requires far higher temperatures (300°C), is not difficult to assume that using sonication technology could greatly enhance the comparatively milder NaOH treatment method. The application of sonication technology in a continuous system is also the best indicator of the industrial viability of such a system. In conclusion, there are multiple avenues to explore in future research on using sonication to improve monazite extraction, both with regard to the actual mechanism and the scale up.

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APPENDIX A SAMPLE CALCULATIONS FOR LEACHING

Below is an example of the calculations for a leaching experiment.

A. I

Initial mass (m_{initial})	8g
Liquid-Solid Ratio (LS)	7 mL/g
Total Solution Volume (V_{sol})	56 mL
Concentration by mass ($x_{\text{H}_2\text{SO}_4}$)	45% (%m/m)
98% H_2SO_4 Added ($V_{\text{H}_2\text{SO}_4}$)	17.54 mL
Density of 98% H_2SO_4 ($\rho_{\text{H}_2\text{SO}_4}$)	1.83 g/cm ³
Water Added ($V_{\text{H}_2\text{O}}$)	38.46 mL
Density of Water ($\rho_{\text{H}_2\text{O}}$)	1.00
Final mass (m_{residue})	7.396g

In order to prepare 56mL of 45% m/m H_2SO_4 using 98% H_2SO_4 and distilled water we use the equations:

$$\frac{m_{\text{H}_2\text{SO}_4}}{\rho_{\text{H}_2\text{SO}_4}} = V_{\text{H}_2\text{SO}_4} \quad (35)$$

$$\frac{m_{H_2O}}{\rho_{H_2O}} = V_{H_2O} \quad (36)$$

$$V_{H_2SO_4} + V_{H_2O} = V_{sol} \quad (37)$$

$$\frac{m_{H_2SO_4} * 0.98}{(m_{H_2SO_4} + m_{H_2O})} = x_{H_2SO_4} \quad (38)$$

Therefore

$$\frac{m_{H_2SO_4} * 0.98 * (1 - x_{H_2SO_4})}{x_{H_2SO_4}} = m_{H_2O} \quad (39)$$

Now insert equation 35, 36 and 39 into equation 37:

$$\frac{m_{H_2SO_4}}{\rho_{H_2SO_4}} + \frac{m_{H_2SO_4} * 0.98 * (1 - x_{H_2SO_4})}{x_{H_2SO_4}} = V_{sol} \quad (40)$$

Allowing us to solve for $m_{H_2SO_4}$ and calculate $V_{H_2SO_4}$ and V_{H_2O} .

Once the experiment was completed and the samples analysed by the XRF, the recovery calculations were made according to equation 32:

$$yield = \left(\frac{m_{initial}c_{x,initial} - m_{residue}c_{x,residue}}{m_{initial}c_{x,initial}} \right) * 100 \quad (32)$$

A. 2

Element (x)	Feed concentration (C _{initial})	Residue Concentration (C _{residue})
Cerium	27.542	26.13
Neodymium	16.558	15.944
Lanthanum	8.947	8.455

So for cerium the calculation becomes:

$$yield (\%) = \left(\frac{8g * 27.54 - 7.396 * 26.13}{8g * 27.542} \right) * 100 = 12.29\% \quad (41)$$

APPENDIX B RESULTS FOR REACTOR GEOMETRY

Below are the results for REE extraction for:

1. Setup 1: 250mL jacketed beaker with the probe positioned at the middle of the reactor
2. Setup 2: 250mL jacketed beaker with the probe positioned 3cm from the bottom
3. Setup 3: 400mL jacketed beaker (wide) with the probe positioned 3cm from the bottom

The reaction conditions for all three experiments were as follows:

B. I

Initial mass (m_{initial})	15g
Acid Strength (%m/m)	60%
Liquid-Solid Ratio (LS)	7 mL/g
Sonication Power (W)	94W
Sonication time	30 minutes
Stirring rate	450 RPM
System Temperature	60°C

B. 2

REE Recoveries			
Element	Setup 1	Setup 2	Setup 3
Cerium	8.95	34.98	39.46
Lanthanum	10.92	37.46	42.47
Neodymium	5.86	28.11	34.5