

Gas phase metal extraction case study: The extraction of iron from iron(III) oxide

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Extraction processes that utilise organic ligands in the gas phase differ from conventional energy intensive pyrometallurgical processes as well as harsh chemical extraction techniques, in the sense that it is less energy intensive and the possibility exists to recover and reuse the ligand. Even though the technology was first proposed in the 1980s, little is known about the reaction kinetics and practical applications of such processes. As part of an ongoing investigation into the application of gas phase extraction, the extraction of iron from iron(III) oxide was studied in a fluidised bed. The reaction conditions were varied to study the influence of reaction temperature, ligand concentration and metal oxide concentration on the extraction kinetics. At low iron(III) oxide concentrations more than 80% of iron was successfully extracted after 4hrs using the ligand, acetylacetone. It was also found that all three reaction variables have an influence on the extraction kinetics.

Keywords: Extractive metallurgy; leaching; iron(III) oxide; acetylacetone

INTRODUCTION

Gas phase extraction of metals refers to process technology first described by Cox and co-workers (1985). The process, also referred to as the SERVO process (Allimann-Lecourt, 2002), have been used on a laboratory scale to extract heavy metal contaminants

from low grade ore (Duke, 1985), sediment (Allimann-Lecourt, 1999), spent catalysts and fly-ash. A metal bearing ore/ waste material, which contains a metal present as an oxide, hydroxide, or sulfide, is heated in a fluidized bed and subjected to fluidization by a volatile organic chelating acid and a carrier gas (optional). The extractant reacts selectively with the targeted metal to produce a volatile metal-extractant complex. The product is carried away from the reaction zone and the metal can be recovered by reduction for example, while the volatile organic chelating acid is recycled (Duke, 1985).

Conventional metal extraction processes include pyrometallurgical processing and hydrometallurgical processing. Pyrometallurgical processes cannot be applied to low grade ore sources without concentration, it produce “green house gasses” and require large amounts of energy. Hydrometallurgical processes, although applicable to low grade metal sources, usually comprise of conventional leaching that are usually non-selective and subsequent complicated recovery processes are required. The final recovery from solution give rise to additional process equipment and the leaching liquor is usually a harsh chemical and non-recyclable after recovery of the metal.

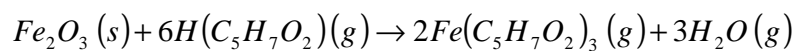
Gas phase extraction offer a possible solution to the limitations mentioned above. It has been shown by Duke (1985) that very selective volatile organic chelating extractants can be developed for specific applications. Even if several metal volatile metal complexes are formed, a series of temperature controlled condensers can be used to produce clean gas streams as these metal complexes have different crystallization and condensation temperatures (Berg and Hartlage, 1964; Alliman-Lecourt, 2002). If hydrogen reduction

is employed to recover the metal, the acidic extractant is regenerated and the metal obtained in its elemental form.

In order to obtain a better understanding of the reaction kinetics of the gas phase extraction process, our group has been studying the influence of the reaction conditions on the extraction of iron from iron(III) oxide. A study is also currently under way to determine the reduction conditions of iron.

IRON EXTRACTION

The global demand for iron is increasing and the economical and technologically feasible iron reserves are being depleted. Gas phase extraction of iron with acetylacetone (Fig 1) offer a possible solution to this problem, as the technology allows the extraction of iron from various alternative iron sources. A few examples can include the recovery of iron from spent iron oxide catalyst, coal mine sludge, tailings that contain a significant amount of iron, red mud (waste stream from the Bayer process), etc. Iron(III) oxide reacts readily with acetylacetone (Allimann-Lecourt *et al.*, 1999) and the reaction equation is given below:



Acetylacetone is vapourized at its boiling point (140°C) and send through a bed of iron bearing material. The flux of the ligand fluidises the bed and the solid gas reaction takes place, forming a volatile iron(III) acetylacetonate complex. The fluidisation allows excellent gas/ solid contact to improve extraction kinetics. Iron(III) acetylacetone melts at 173°C and the solid volitalize between 92 – 275 °C (Potgieter et al., 2005). The

temperature in the fluidised bed is kept below the decomposition temperature of iron(III) acetylacetonate. The extraction product, iron(III) acetylacetonate, can be recovered and sold, or subjected to reduction for iron recovery while the acetylacetonate is recycled back to the process.

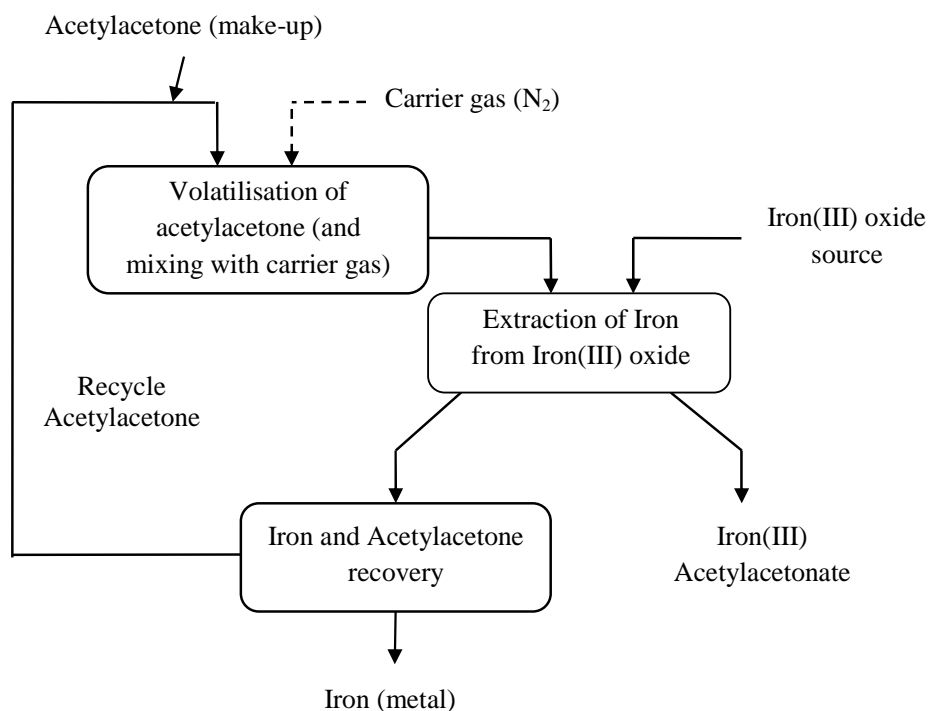


Figure 1 Gas phase Iron Extraction

EXPRIMENTAL

The gas phase extraction kinetics of iron(III) oxide were studied by varying the reaction temperature, acetylacetonone ligand flow rate and metal concentration. A 50g mixture of silica and iron(III) oxide of various iron concentrations (1, 3, 10 wt %) was subjected to extraction by vapour phase acetylacetonone at different ligand flow rates (1 mL/min and 3 mL/min) and various reaction temperatures (190°C, 210°C, 230°C and 250°C). A detailed description of the experimental setup and conditions is given by van Dyk et al. (2010).

RESULTS AND DISCUSSION

The influence of the reaction temperature on the extraction kinetics were studied for different weight percentages of iron(III) oxide. The reaction temperatures that were used are 190, 210, 230 and 250 °C. The cumulative iron extraction with time for 1 wt% iron(III) oxide load and 1 mL/min acetylacetone flowrate is presented in Fig 2.

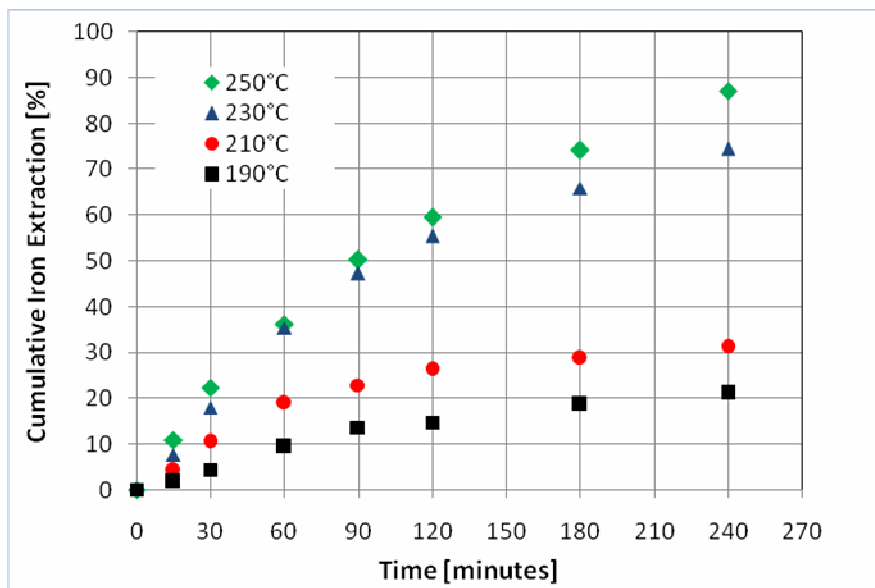


Figure 2 Iron Extraction with time at different temperatures for 1 wt% iron(III) oxide load and 1 mL/min acetylacetone (van Dyk et al., 2010).

It can be seen that the extraction increase with an increase in temperature. The highest extraction, 87%, was obtained for 1 wt% at 250°C after 4hrs. As the temperature increase the initial reaction rate increases significantly up to 230°C. This can be seen by the large difference in iron extraction between 190°C and 230°C. The influence of temperature above 230°C is much lower and a possible reason for this might be that diffusion through a product layer can limit the reaction rate at temperatures below 230°C. As the temperature increase not only does the chemical reaction rate increase, but also the

rate of vaporization of the product, increasing the rate of diffusion through a product layer. Similar temperature dependencies were observed for the 3 wt% [1 mL/min] and 10 wt% [1 mL/min] iron(III) oxide loads, however, the influence of temperature was less significant. In general it can also be seen that the rate of reaction decrease as the reaction progress and the metal oxide particle is consumed, thus reducing the surface area available for reaction.

If one compares the extraction time behaviour of iron extraction (Fig 3) for 1 wt% iron(III) oxide load with that of higher loads (3 wt% and 10 wt%) at the same reaction conditions (250°C, 1 mL/min), it can be seen that there is a decrease in the initial extraction rates. The iron extraction decrease from 87% to 29% after 4 hours reaction time when the load of iron(III) oxide is increased from 1 wt% to 10 wt%. However, the actual amount of iron(III) oxide that reacted when 10 wt% of iron(III) oxide was used, is about three times higher than for the 1 wt%. In the case of 10 wt% iron(III) oxide, the surface available for reaction is higher than when 1 wt% is used as more particles are present. The reaction efficiency thus increased due to a higher initial available surface area or iron(III) oxide concentration.

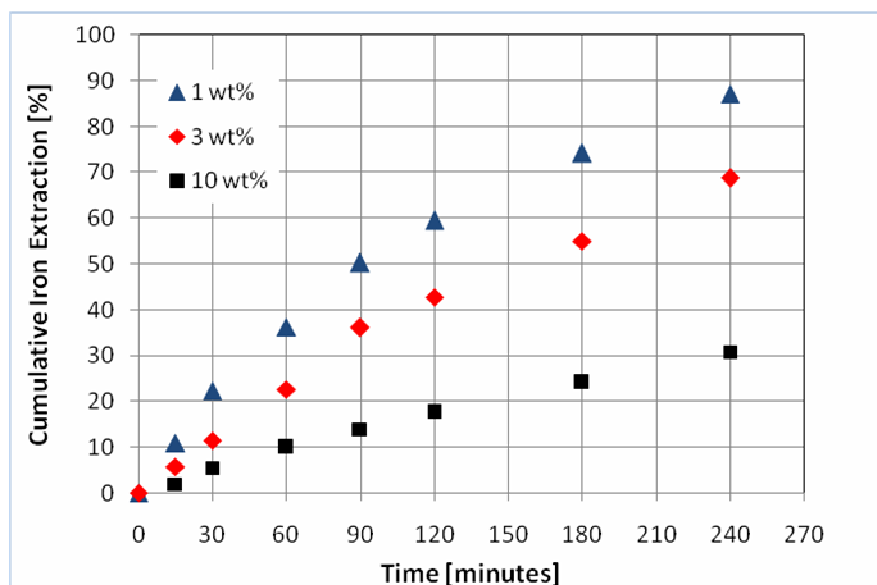


Figure 3 The influence of iron(III) oxide load on the extraction of iron with time at 250°C and 1 mL/min acetylacetone.

Additional experiments were carried out at a higher ligand flow rate of 3 mL/min and 250°C for the higher concentration mixtures (3 wt% and 10 wt%) to determine the influence of the ligand flow rate on the extraction kinetics. The results for the first 120 minutes reaction time are presented in Fig 4.

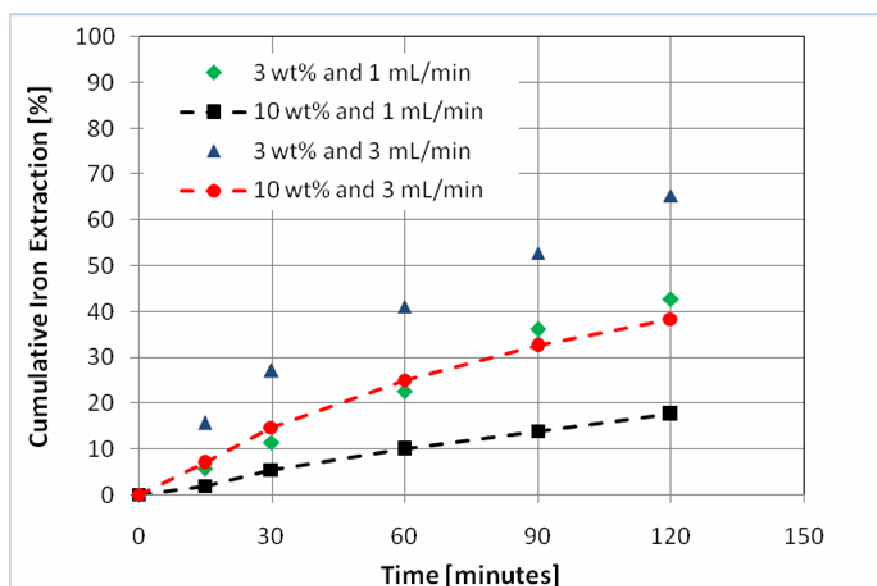


Figure 4 The influence on acetylacetone flow rate on the extraction of iron with time at 250°C and different iron(III) oxide loadings.

By increasing the acetylacetone flow rate an increase in the reaction rate, as well as, the amount of metal extracted can be achieved. For a 10 wt% iron(III) oxide load, the extraction increase from 30 % to 59% after 4 hrs. Potgieter et al. (2005) showed that a maximum of 75% of iron extraction can be achieved after 45min at 180°C from a 3 wt% Fe₂O₃ charge with an acetylacetone flow rate equal to 6 mL/min. These results confirm that the acetylacetone flow rate play a significant role in the reaction kinetics. It should be noted that the molar flux of acetylacetone is well above the stoichiometric ratios of the reaction. According to Habashi (1980) the overall rate of reaction of chemically controlled processes are independent of the gas flow rate, while diffusion-controlled process depends on the gas flow rate. Kinetic modelling proved to be challenging as the reaction kinetics of the extraction of iron from iron(III) oxide depend on a combination of rate limiting steps, depending on the reaction conditions.

CONCLUSIONS

It has been shown that gas phase extraction can be used for iron extraction from iron(III) oxide using acetylacetone as a volatile organic chelating extractant. The reaction kinetics is temperature dependent, and at low temperatures volatilization of the product layer may affect the overall reaction rate. There exists an interrelatedness between the influence of iron(III) oxide concentration and the ligand flow rate on the reaction kinetics. With the gas phase extraction process, 87% iron could be extracted from a 1 wt% iron(III) oxide

mixture after 4 hrs. This technology is thus suitable for iron extraction from low grade iron sources.

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