

REVIEW OF THE IRON RECOVERY PROCESSES FROM LADEN LEACH LIQUORS IN HYDROMETALLURGY

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ABSTRACT. Iron is usually present in higher concentrations in the laden solutions and its removal and elimination to a stable phase is a severe problem in hydrometallurgy. This article analyses and compares the processes of solvent extraction and ion exchange as methods for the iron separation and concentration in a sufficient amount, which would enhance its further removal to products with potential for application to other industries. The factors affecting the goethite, hematite and magnetite processes and the area of use of the produced iron oxides are reviewed.

Keywords: iron, processing, hematite, magnetite, hydrometallurgy

Introduction

Iron is the fourth most abundant element in the Earth's crust, where it exists mainly in four different types of minerals – oxides, sulphides, silicates, and carbonate. The soluble forms of iron are two – ferrous and ferric iron ions as the direction and rate of the relevant oxidation-reduction process strongly depend on the environment's pH and redox conditions. Ferrous iron is a product of reducing processes, and it oxidises abiotically with high rate at pH above 3,5 in the presence of oxygen, and bacterially at acidic and neutral pH. Some bacterial strains oxidise ferrous iron even at anaerobic conditions. Ferric iron is a product of the oxidation process, its solubility steadily decreases at pH above 3,0, and it precipitates as iron hydroxides. Iron oxides divide into two subgroups – a subgroup of minerals consisting of ferric iron, such as ferrihydrite ($\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$), goethite ($\alpha\text{-FeOOH}$), hematite ($\alpha\text{-Fe}_2\text{O}_3$), for example. The second subgroup of iron oxides consists of ferric and ferrous iron, such as magnetite (Fe_3O_4) and green rust ($\text{Fe}_x^{\text{III}}\text{Fe}_y^{\text{II}}(\text{OH})_{3x+2y-2}\text{SO}_4$). Siderite (FeCO_3), typical for sedimentary rocks, and pyrite (FeS_2), found in sedimentary and metamorphic rocks, are examples of iron-containing minerals formed at anaerobic conditions. Because of that minerals variety, it is not surprising that most of the non-ferrous metals (Cu, Ni, Zn) form common sulphides and oxides with iron. As a result, the iron follows the base metals' route while processing the relevant raw materials. For example, iron (as sulphides) accumulates during the flotation process, and its content in the concentrate can reach up to 29 % (Neale et al., 2009).

Ferric/ferrous iron plays a crucial role in oxidative/reductive leaching of secondary sulphide and electronic scrap (Dev et al., 2020) and refractory cobaltic ores and manganese oxides (Das et al., 1982), respectively. The base metal leaches and concentrates in the laden leach liquor, which requires the activities for iron removal and recovery of the valuable element to be applied. Because of higher annual demand of various base metals and rare-earth elements due to the constant growth of the electronic industry, the need for the processing of raw materials and industrial wastes with complex content and mineralogy arises (Chang et al., 2010; Parhi et al., 2015, Georgiev et al., 2018) however, in accordance with strict environmental regulations and applying the principles of the circular economy.

To review the main techniques for the iron removal from laden leach liquors such as solvent extraction, ion exchange,

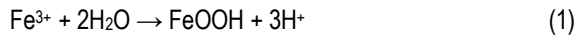
iron precipitation as well as the fate and area of application of produced iron (hydrous) oxides is the main aim of this article.

Precipitation technique

That kind of iron removal technique is based on the direct precipitation of different (hydrous) oxides without the preliminary application of methods for the metal separation to its stream. The main advantage of that approach is the significant simplification of the laden solution flow-sheet and no need to use expensive chemicals, some with toxic properties. It could be applied to two different acidic solutions in which the iron concentration ranges from several hundred milligrams to several dozens gram per litre. Laden leach liquors (LLL) generated from the hydrometallurgical processing of raw materials is the first type of solution to which the approach is applied. The iron concentration can reach several dozens gram per litre in those solutions as the ferrous iron is the dominant valency state. Apart from iron, the substantial concentration of base metals (copper, nickel, zinc), LLL contains silica, sulphates, and aluminium as well. The direct precipitation requires preliminary ferrous iron oxidation combined with a partial acid neutralisation to a specific pH endpoint. Thus, the process is realised in a chemical reactor, and air (in a combination of copper ions as a catalyst), or sulphur dioxide could be used as a chemical oxidant most frequently. The products of the iron removal process strongly depend on the conditions under which the process has been carried out, such as iron oxides with a crystalline structure (goethite ($\alpha\text{-FeOOH}$), akaganeite ($\beta\text{-FeOOH}$), lepidocrocite ($\gamma\text{-FeOOH}$), hematite ($\alpha\text{-Fe}_2\text{O}_3$), maghemite ($\gamma\text{-Fe}_2\text{O}_3$)) (Wang et al., 2011) or iron hydrous oxides as schwertmannite ($\text{Fe}_{16}\text{O}_{16}(\text{SO}_4)_2(\text{OH})_{12}$) and ferrihydrite ($5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$) with poorly crystalline structure (Loan et al., 2006). In the latter case, the precipitated iron oxides are with low economic value due to the iron content being lower than 50%, and they are usually deposited at sites for long-term storage of technogenic wastes (Table 1). So nowadays, goethite process (Allen et al., 1970; Bodson, 1972), hematite process (Mealey, 1973), paragoethite process (Cubeddu et al., 1996), and Zincor process (Meyer et al., 1996) are the main processes applied at an industrial scale, as the latter two are used in the zinc industry only (Loan et al., 2006).

Goethite process

The goethite precipitation proceeds according to the following hydrolysis reaction:



as the ferric iron concentration in the solution must not exceed 1 g/ L. The process takes place at a higher temperature (80-90°C) and pH 2-3. Goethite precipitation requires precise monitoring and control between the ferrous iron oxidation (acid-consuming process) and ferric iron precipitation (acid-generating process) as the net reaction is acid generating:



For that reason, both processes are separated into two reactors – a reactor for chemical oxidation of ferrous iron and a reactor for goethite precipitation as the feeding rate of the second reactor is equal to the rate of goethite deposition. Usually, slower precipitation rates are applied because they favour the production of well-crystallised goethite (α -FeOOH) while the higher precipitation rates lead to the formation of akaganeite (β - FeOOH) (Agatzini et al., 1986; Langova et al., 2007). Despite the same chemical formulae, goethite and akaganeite possess a different crystal structure, which has a strong effect on their properties, such as their filtration rate. For example, akaganeite is characterised by a hollandite structure based on body-centred cubic packing of anions. The specific gravity is 3,52 g/ cm³ (Cornell and Schwertmann, 2003).

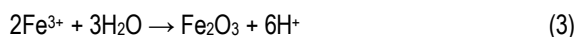
Table 1. *The primary type of iron precipitates formed during the iron removal from laden leach liquors of hydrometallurgical processing of zinc concentrate (Onozaki et al., 1986; Piret and Melin, 1993; Ashman, 1996)*

Characteristic	The technique of iron precipitation		
	Jarosite	Goethite	Hematite
	A.Fe ₂ (SO ₄) ₃ (OH) ₆ A = H ⁺ , K ⁺ or Na ⁺	α - FeOOH	α -Fe ₂ O ₃
Iron content, %			
Theoretical	30-35	62.9	69.9
Practical	25-30	40-45	50-60
S content, %	10	5-8	2-5
Zn content, %	4-6	8	0,5-1,0

Akaganeite is practically unfilterable, and for that reason, its formation as the main product is undesirable at industrial scale operation. Goethite is characterised by an orthorhombic structure based on close hexagonal packing of anions; the specific gravity is 4,26 g/ cm³. Its filtration rate usually is within the range of 80-90 mL/ min, and that is also a reason for the broad application of goethite precipitation at an industrial scale (Cohen et al., 2005).

Hematite process

The hematite precipitation proceeds according to the following reaction:



This reaction takes place at a higher oxidising environment ($p\text{O}_2 > 5$ bar) and temperatures above 185°C (Ropenack, 1982). Hematite is an iron oxide with deep red colour. It is characterised by a compact crystal structure of corundum type; the specific gravity is 5,26 g/ cm³. Its filtration rate varies in the range of 40-130 mL/ min, depending on the impurities content (Cornell and Schwertmann, 2003).

The hematite process is carried out in sulphate as well as chloride solutions. However, the exact mechanism of hematite precipitation is quite different. The content of hematite in sulphate media strongly depends on the amount of free sulphuric acid generated during the hydrolysis process. For example, at a temperature higher than 200°C, when the concentration of sulphuric acid reaches the limit of 65 g/L, FeOHSO₄ is the main product of the precipitation process (Umetsu, 1977). At a lower acid concentration, a mixture of FeOHSO₄/ Fe₂O₃ obtained. So, the regular removal of the generated acid, such as neutralisation, controls the way of ferric iron precipitation. The boundary limit of sulphuric acid for hematite formation decreases almost linearly with the temperature decrease at which the process is carried out. The main advantage of the hematite process is that the presence of a higher concentration of base metals (in the range of 60 – 100 g/L) increases the boundary between Fe₂O₃ and FeOHSO₄ to a higher acid concentration at the same temperature.

The hematite precipitation from chloride solutions was studied by Dutrizac and Riveros (1999) at temperatures below 100°C, ambient pressure and in combination with seeding. The researchers proposed two different mechanisms of hematite formation. The first mechanism took place at 100°C without seeding with Fe₂O₃, and akaganeite (β -FeOOH) was the product of iron precipitation. However, akaganeite is a metastable phase at those conditions, and it transforms into hematite at a prolonged time. Iron precipitates to hematite directly when the process takes place at a lower temperature (60°C) and the seeding rate is in the range of 10-20 g/ L. The percentage of iron removal is almost 100%. Temperature and pH have a substantial effect on the precipitates' colour and filtration (Masambi et al., 2016). The deepest red colour, typical of hematite, is produced at lower pH (1,0) and higher temperature (80°C). Increasing the pH and decreasing the temperature lead to precipitates with substantial brown colour with an insufficient pigmentary characteristic. However, the filtration rate improves in the same direction due to the reduced zeta potential of fine particles and further agglomeration.

The higher iron content (Table 1), chemical stability and density of hematite qualify it as a by-product that can be used as a raw material for the production of iron, steel, or pigments according to the impurity content (Masambi et al., 2016).

Paragoethite process

Despite its name, this process is carried out at conditions completely different from conditions at which the goethite process takes place. For example, the ferric iron concentration is in the range of 12-16 g/ L; the temperature is in the range of 80 – 85°C, the initial pH is 1.0, while the final pH is 3.5. Not surprisingly, ferrihydrite (Fe₃HO)₈.4H₂O and schwertmannite [Fe₈O₈(OH)₆SO₄] are the main iron phases formed at those conditions (Loan et al., 2006):



Besides these two minerals, jarosite, silica, and poorly crystalline goethite are also detected (Claassen et al., 2002). Schwertmannite and ferrihydrite are characterised by brownish-yellow to dark brown colour and very similar specific gravity (3,77 – 3,95 g/ cm³) (Cornell and Schwertmann, 2003). The main advantage of that iron removal process is the higher rate of laden leach liquor processing with no strict limits about the ferric iron concentration. Thus, the process is applied in the

hydrometallurgical processing of zinc raw materials where zinc ferrite ($\text{ZnO}\cdot\text{Fe}_2\text{O}_3$) is formed as a stage of their processing. However, the drawback of the primary process is the lower filtration rate of iron residue due to its size, crystal structure, and specific gravity.

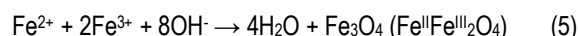
The selection of the appropriate iron removal process strongly depends on the non-ferrous metal-containing in LLL so that its losses through sorption/ co-precipitation during the iron precipitation will be at acceptable levels. The magnitude of these processes depends on the experimental conditions at which the iron removal is carried out (temperature, the endpoint of pH neutralisation, iron: base metals ratio in the liquor). For example, the nickel losses from acidic leach liquor of lateritic nickel ore by co-precipitation with goethite could be restricted around 4% when the endpoint of pH neutralisation is 2.5. If the pH is maintained at 3.0, the nickel losses increased to 15.9% (Chang et al., 2010). In the same way, the lowest nickel and copper losses during hematite precipitation were measured at conditions most favourable for its formation (pH-1.0, t-80°C). Any changes from those conditions lead to higher losses, for example, 13.2% for nickel and 11.9% for copper at 60°C (Masambi et al., 2016). In both cases, base metals losses were permanent because their ions co-precipitated within the iron oxides' crystal structure, and the base metals backwashing from the iron residue with a weak acidic solution was not efficient. On the contrary, the residues from Paragoethite and Zincor processes retain a substantial amount of zinc because of their higher surface area and the zinc losses could be restricted significantly employing adequate acidic washing (Zinck and Dutrizack, 1998; Loan et al., 2006).

Treatment of acid mine waters (AMW) is the second direct application of precipitation technique of the iron removal in practice. AMW is generated as a result of spontaneous *in situ* processes of bacterial and chemical oxidation of sulphides due to their contact with molecular oxygen. Acidic pH, a higher concentration of iron, sulphate and aluminium up to 3-4 g/L and content of non-ferrous metals (most frequently, copper and/or zinc) several times higher than the maximum admissible levels for waters applicable in industry and agriculture are the typical characteristics of these waters. Acid mine waters are a serious environmental problem in areas with abandoned mines, and their treatment by passive systems is the only reasonable way, both from an economical and technical point of view. The method of neutralisation of water acidity is a crucial process for iron removal. It could be organised in different ways having in mind the pollutant concentration. For example, depending on the value of ferrous: ferric ratio the neutralisation of AMW could be realised at aerobic conditions (open limestone channel, at lower values of Fe^{2+} : Fe^{3+}) and anaerobic conditions (anoxic limestone drains, at higher values of Fe^{2+} : Fe^{3+}) (Favas et al., 2016). In the first case, the slightly acidic pH, due to the acidity neutralisation, trigger the chemical oxidation of ferrous iron to the ferric state. The ferric iron ions precipitate as goethite mostly. At anaerobic conditions and slightly alkaline pH, the ferrous iron precipitates as siderite (FeCO_3) and pyrrhotite ($\text{Fe}_{(1-x)}\text{S}$). When the iron concentration in AMW is lower than 50 mg/L, the treatment is carried out in aerobic wetlands directly without a detrimental effect on the water chemistry and the biological processes of that type of ecosystem. In that case, the degradation of organic residues plays a leading role in the neutralisation of the hydrolytic acidity (Batty et al., 2008).

The process of iron hydrolysis/precipitation and ferric iron hydrous oxides formation combines with sorption or co-precipitation of other pollutants contained in mine waters (such as sulphate, aluminium, toxic elements, and some amount of non-ferrous metals). The endpoint of pH neutralisation and the molar ratio between iron and other pollutants are the key factors that control the rate and extent of sorption/co-precipitation processes. For example, the iron precipitates as goethite, mainly when the endpoint of pH neutralisation is lower than 5.0 (Fish et al., 1996) with minimal co-precipitation of silica and gypsum. The generated rich-in-iron-sludge (the content of iron oxides is higher than 50%) is with satisfactory pigmentary characteristics, and it is used as a raw material for the production of mineral pigments for industry (Hedin et al., 2002). If the endpoint of pH neutralisation of AMW is above 5.5, the generated rich-in-iron-sludge is with weak pigmentary characteristics due to the less than 50% content of iron oxides. It requires their removal periodically from the passive system and long-term storage at a tailing.

Magnetite process

Magnetite is an iron oxide with black colour characterized by an inverse spinel structure and ferrimagnetic properties due to the presence of ferrous and ferric iron in its structure. Its specific gravity is 5.18 g/cm³ (Cornell and Schwertmann, 2003). The magnetite precipitation proceeds according to the following reaction:



The process takes place in alkaline pH (9-11), atmospheric pressure, and temperature in the range of 60 – 100°C (Rabelo et al., 2001; Jolivet et al., 2004). Thus, the magnetite process is suitable only for rich-in-iron technogenic solutions with acidic pH, which are generated after the preliminary iron separation and concentration from the other components of laden leach liquor through an ion exchange resin/ solvent extraction technique. Anaerobic conditions are obligatory, as well as the accurate monitoring and control of the ferrous oxidation enabling the maintenance of the exact ratio between ferrous to ferric iron (2:1) in the reactor. The average size of the obtained magnetite nanoparticles ranges between 10-15 nm up to 25-30 nm (Wei & Viadero, 2007; Zhang et al., 2015). Their form is cubic or spheroidal. Magnetite nanoparticles find applications in biomedicine, nano-sorbents and environmental engineering, controlled drug delivery, and ferrofluid technology (Gupta and Wells, 2004; Mak and Chen, 2004; Love et al., 2005).

2. Techniques for separation and concentration of iron from LLL before the application of precipitation methods

The development and applicability of hydrometallurgical methods at an industrial scale depend on the presence of effective methods for separation and concentration of base metals from laden leach liquors. The process of cementation on the surface of zero-valent metal was widely applied into the practice at the beginning (Ahmed et al., 2011). Over the years, it has been replaced by processes of ion exchange and solvent extraction. Both alternatives are based on using highly selective reagents towards relevant elements, which react at higher rates in both directions - the processes of concentration and elution (stripping) of ion exchange resin or organic solvent, respectively.

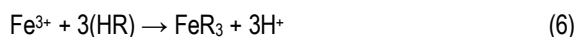
As a result, the methods of ion exchange and solvent extraction have had a strong positive effect on the further development of hydrometallurgy, and its application in the processing of a wide range of raw materials (ores, concentrates, technogenic wastes or electronic scrap) enriched not only with non-ferrous metals but also with rare earth elements.

Ion exchange processes

The chelating ion exchange resins suitable for iron ion exchange are divided into five main classes according to their chemical content: iminodiacetic, picolylamine, sulphonated diphosphonic, sulphonated phosphonic, and aminophosphonic. All these classes have a stronger affinity to ferric iron in comparison to the ferrous iron form (McKevitt and Dreisinger, 2009).

The phosphonic acid group (PO_3H_2) based on chelating ion exchange resins are widely used in practice and are known under the trade names LEWATIT (Guide, 2012), Purolite (Lenntech), and Dyphonix (Chiarizia et al., 1997). Their most important advantage is the high degree of selectivity to iron because of the complexes formed between the resin's reactive part and ferric iron (a stage of loading), instead of just ionic bond, and its capability of complete regeneration (a stage of elution). This method applies to technogenic solutions laden with higher concentrations of valuable ions as copper, cobalt or nickel (Lee and Nicol, 2007; McKevitt and Dreisinger, 2009).

The reaction between the protonated form of the phosphonic group and ferric iron proceeds according to this equation:



Temperature, pH, acidity concentration or the type of ion exchange resin have a substantial effect on the iron adsorption, and their impact is studied using batch and continuous flow experiments. The parameters determined by batch tests are:

- 1.) The total amount of iron adsorbed by the resin at equilibrium, q_i (in mg/g resin), i.e. the state at which the whole resins adsorption capacity is exhausted;
- 2.) Percentage of iron removed from laden leach liquor due to adsorption by the chelating resin, S (in %);
- 3.) Distribution coefficient, i.e. effectiveness of ion exchange resin to remove and adsorb a particular ion from the solution, K_d ;
- 4.) The separation factor that describes preferences of resin to iron in contrast to each base metal from the processed liquor, i.e. a ratio of iron-loaded to each base metal loaded.

For example, the experiments carried out by Izadi et al., (2017) revealed that the maximum adsorption capacity of Purolite S957 to iron from industrial copper raffinate solutions was 42 mg Fe/g resin. The equation rate with pseudo- n^{th} order and Langmuir-Freundlich model predicted the kinetics and equilibrium data of the ion exchange process.

The parameters determined by continuous flow experiments (fixed bed studies) are:

- 1) The efficiency of column adsorption at the tested flow rate, %;
- 2) Breakthrough time, i.e. the time needed for the resin surface's saturation so that the outlet iron concentration of column becomes 0,3 % of the inlet.

The adsorbed iron eluted completely at acidic pH, which regenerates the initial resin's adsorption capacity. So, the metal separates and concentrates in a separate technogenic stream, a precondition for the iron recovery to products applicable for

other industries. The elution process can be carried out with sulphuric or hydrochloric acid according to the pH and the method for iron precipitation. However, in both cases, acid consumption is significant, and it ranges between 5 – 7 g acid/g resin depending on the type of resin and the experimental conditions at which the process takes place (Zhang et al., 2016; Izadi et al., 2017). The regeneration stage could be carried out in the presence of a suitable reducing agent (SO_2 , CO or oxalic acid for example) which reduces ferric iron to ferrous state as the latter liberates quickly from the resin's surface at slightly acidic pH (Lee and Nicol, 2007; Zhang et al., 2016). So, acid consumption could be reduced significantly, which is a significant advantage for those cases where the precipitation is carried out at highly alkaline pH.

Solvent extraction process

This is the second option that is used to separate and concentrate iron in its stream before its recovery as the relevant iron (hydrous) oxide. The process is carried out in two stages – extraction and stripping. The extraction stage relies on a mixture of appropriate diluents (such as kerosene, toluene, xylene or *n*-octane) and a suitable organic compound, mostly organophosphorus acids, which form a strong bond with ferric iron from leach liquor. Among the organophosphorus acids, DEHPA ((di-2-ethylhexyl) phosphoric acid) is the most widely used. Because of the acidic properties, the extraction ability of D2EHPA strongly depends on the extent of preliminary neutralisation with NaOH. Apart from iron, some base metals, zinc mostly, are co-extracted too (Azizorghaben et al., 2016), as the experimental conditions (concentration, organic to aqueous phase ratio and pH) affect the process's rate. The efficiency of solvent extraction (E , %) and the distribution coefficient between the two phases (D) describe the removal of each metal. The separation factor (β) between iron and the co-extracted base metal describes the reagent selectivity at the relevant experimental conditions. For example, the lower value of $\text{pH}_{\text{equilibrium}}$ (in the range of 0.9 – 1.1) increases the amount of the extracted ferric iron on account of zinc, which affects the value of separation factor ($\beta_{\text{Fe}/\text{Zn}}$) (Georgiev et al., 2018).

The main drawback of using D2EHPA as a ferric iron extractant is the need for a highly acidic solution (such as 5 – 6 M) for the stripping stage. It has a substantial limitation for further processing of the rich-in-iron stream. The preliminary reduction of ferric iron to ferrous state is the option to carry out the iron stripping in a slightly acidic solution (0,07 – 0,15 N). Oxalic acid (Akhlaghi et al., 2010), molecular hydrogen (Demopoulos, G., Gefvert, D. 1984), and some metals in zero valency state (galvanic reduction) (Chang et al., 1996; Sun and O'Keefe, 2002) are the most studied reducing compounds for that purpose.

Conclusions

Processing of raw materials with complex chemical content and mineralogy, stricter environmental regulations and ideas of the circular economy are the factors that set the growing role of the ion exchange and solvent extraction in iron recovery from laden leach liquors. Both methods produce rich-in-iron technogenic solutions, making possible iron oxides with preliminary fixed characteristics to be generated with the relevant iron precipitation technique application.

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