

# **Extractive Metallurgy 2**

*Metallurgical Reaction Processes*

**Alain Vignes**



**ISTE**

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# Preface

Extractive metallurgy is the art of extracting metals from their ores and refining them.

This book deals with the processes, operations, technologies and processing routes of extractive metallurgy, i.e. the (production) extraction of metals from ores, concentrates (enriched ores), scraps and other sources and their refining to liquid metals before casting or to solid metals.

In many books dealing with metallurgy, the introduction starts by recalling the steps of the progress of metallurgy. These steps, according to and since Lucrèce, are identical to those of human progress: the copper age, the bronze age, the iron age, the silicon age<sup>1</sup>. According to Mohen<sup>2</sup>, the considerable role attributed to the three principal metals in the development of human societies must not be overstressed or overvalued. It is nonetheless true that “metallurgy is the most advanced prehistoric manifestation of the mastery of natural resources” (Mohen). Extracting copper from its ore dates back to the middle of the fifth millennium before our age and extracting iron from its ore dates from the beginning of the second millennium before our age.

The winning (production) of metals and alloys today is still one of the basic industries of the transformation of matter. Metals and alloys still are essential resources for metallic, mechanic, electromagnetic, electric and even electronic industries (silicon is treated as a metal).

This industry is characterized by:

- Production (of primary metal) ranging from 1,345 million tons (Mt) of steel a year to 138,000 tons of titanium, in 2007<sup>3</sup>.

**Table 1.** *World Metal Production in 2007*

Steel	Aluminum	Copper	Zinc	Lead	Nickel	Magnesium	Titanium
1,345	38	15.6	10.6	7.0	1.66	0.79	0.138

- Very high growth rates in the years 1950 to 1973, and again since 2000. The production of steel was 200 million tons in 1950. The production of aluminum increased from 2 million tons in 1950 to 10 million tons in 1973, reaching 38 million tons in 2007. If in developed countries the growth in terms of tonnage has strongly slowed in recent decades, this is due to a smaller consumption of these products owing to the increase in mechanical and physical properties of the materials and parts forged from these materials, thus requiring less material for the same usage. However the annual production of steel in China increased from 182 million tons in 2002 to 489 million tons in 2007<sup>4</sup>.

- Production costs varying by a factor of 20 to 25 between steel and titanium. The three principal costs in metal production are investment, ore and energy consumption. The energy consumption is about 20 GJ/ton of steel, 80 GJ/ton of aluminum and 160 GJ/ton of titanium. Hence the permanent research into improvements of the processes or operations and/or the development of new processes.

- Very high recycling rates. Recycled steel represents 46% of iron sources in worldwide steel production. The “electric furnace processing route” produces 35% of steel. It uses 75% less energy than the integrated route. The recycling rate of aluminum represents 25% of total production and the energy consumption from recycled aluminum represents 5% (energy reflow) of energy consumption from the ore. The production of primary zinc is 7.4 million tons and from recycled zinc is 2.1 million tons. In the case of lead, the production from recycled lead is greater than 50%.

- Very high quality products with degrees of purity (i.e. contents of harmful impurities) for the finished products, comparable to the purity of materials for electronics and

with very narrow concentration ranges of the alloying elements, to obtain physical or mechanical properties with very small dispersions. For metal castings reaching 300 tons, steel grades with carbon content of less than 25 ppm, and sulfur and phosphorus content of less than 20 ppm or even 10 ppm can be guaranteed. The impurities in liquid aluminum after electrolysis and refining are <3 ppm for Li, <1 ppm for Ni and <1/10 ppm for H. The contents of each impurity in copper for electric wire must be <1 ppm. Achieving these chemical performances coupled to research into the lowest energy consumption requires perfect mastery of the process and thus a profound knowledge of its technology.

- The energy consumption and reduction of pollution (rejected CO<sub>2</sub>, SO<sub>2</sub> and dust) from the production of metals have become major objectives, leading to the development of new processes or product lines.

- Non-ferrous metal ores often have very low contents of many rare or noble metals, whose extraction and recuperation often constitutes essential steps for the global production economy. Such extraction requires very complex processing routes for recovering rare or precious metals.

Often the metal can or could be produced via several processing routes. The industrial processing routes for a given metal are to a large extent dependent on economic considerations, i.e. the cost of raw materials, cost of energy, cost of equipment and market conditions.

The raw materials for the production of metals and alloys are the ores on one hand and recovered and recycled products on the other:

- the ores. The ores of Sn, Fe, Mn, Cr, Al, Ni are oxides. The ores of many non-ferrous metals, e.g. Cu, Ni, Pb, Zn, Cd, Mo, are sulfides;

- the recycled metals (Fe, Al, Cu, Zn, Pb);



- the steel plant dust containing metals or oxides (Zn, Cd, Pb);
- the residues from leaching operations, e.g. the red muds, a residue containing titanium, vanadium, gallium produced by bauxite leaching during the Bayer process, the gold cyanide sludge;
- the drosses, slags and scoria treated to recover rare metals or to eliminate harmful components.

The operations of mineralogy are known as ore-dressing. In the general case, the ore must be concentrated to free it from minerals of no value, called the gangue, whose main components are oxides ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ). This is done using physical operations: grinding (comminution) or fragmentation of the ore to small sizes to allow easy separation, then separation by sedimentation and enrichment by flotation, magnetic sorting etc., leading to a raw material enriched in components.

The operations of extractive metallurgy treat ores, concentrates and recycled metals. These are mixtures of oxides or sulfides. The processing routes of the ore's treatment, raw or enriched, together with the technologies used in these routes depend first of all on the ore's nature and its metal content.

Thus iron ore is practically pure iron oxide (hematite or magnetite), with a content of iron of the order of 65% and several percent of silica ( $\text{SiO}_2$ ). The basic treatment will be the direct reduction of the iron oxide.

Alternatively, the ores can be treated to give an essentially pure chemical compound of the metal and this compound may be converted to give the metal. For example, aluminum's ore (bauxite), is composed of alumina ( $\text{Al}_2\text{O}_3$ , 30-60%), iron oxide ( $\text{Fe}_2\text{O}_3$ , 1-30%) and silica (1-10%). The first phase of the ore's treatment will be the separation of

these oxides to obtain the pure alumina, which will be reduced in a second phase by electrolysis in molten salts.

The copper sulfide ores, whose copper content is very low, exceptionally reaching 5%, undergo processes of mineralogy (flotation) to obtain concentrates containing Cu (20–25%), Fe (30%) and S (30%). The separation of copper sulfide from iron sulfide via a selective roasting constitutes the first step of the treatment. The second step is a copper converting.

Zirconium ore, zircon (silicate of zirconium and hafnium, i.e.  $\text{ZrSiO}_4$  and  $\text{HfSiO}_4$ ), is converted into gas chlorides whose separation is possible before the reduction of zirconium chloride to very pure zirconium.

Extraction and refining operations may be carried out by pyrometallurgical, hydrometallurgical, halide and electrometallurgical processes:

- *pyrometallurgy* involves processes carried out at high temperatures divided into:

- *primary pyrometallurgy*, which converts the ore or concentrate to impure metal generally in liquid form. The main operations are oxide reduction, sulfide roasting, smelting and converting;

- *secondary pyrometallurgy* is the treatment of the liquid metal, obtained either directly in the first step or by remelting metallic recycled products. It consists of several refining operations, mainly the removal of harmful elements left in the liquid metal (deoxidation, dehydrogenation, etc.) and addition of the alloying elements;

- *hydrometallurgy* consists of operations of primary metallurgy performed in aqueous solutions, at relatively low temperatures and often under high pressure, such as leaching, precipitation and solvent extraction;

- *hydroelectrometallurgy* consists of salt electrolysis in an aqueous solution, yielding the metal in a solid state.

Electrorefining constitutes a refining process of the metal obtained in a first electrolysis;

- *pyroelectrometallurgy* consists of processes employing electrolysis (reduction), either of mattes or oxides (e.g.  $\text{Al}_2\text{O}_3$ ) or chlorides (e.g.  $\text{MgCl}_2$ ) into molten salts, yielding the metal in a liquid state;

- *chlorometallurgy* consists of the following processes:

- *chlorination* of a highly reactive metal oxide, such as titanium or zirconium,

- *separation* of the chlorides via physical processes: distillation and extractive distillation,

- *reduction* of chlorides by metallothermic reduction.

The upholding into operation of an existing processing unit, the improvement of an industrial operation, the implementation of a new technology (not formerly used in the unit) and the development of a new process all fall within technical considerations, as well as economic considerations. In this series, economical considerations will not be discussed, for obvious reasons, but sound economic decisions rest on in-depth technical analyses of the processes and operations. Such in-depth analyses are based on process engineering principles. These methods use mathematical models allowing us to simultaneously take into account the elementary processes and their couplings<sup>5</sup>. These mathematical models are sets of fundamentally-based differential equations derived from thermodynamics, kinetics, heat flow, fluid flow, mass transfer and electromagnetic phenomena. Modeling will thus be at the heart of all the analyses here. The solutions to these differential equations, via analytical or numerical methods, allow us to achieve sound quantitative previsions. Analytical solutions of these equations of partial derivatives have been established in numerous instances, but only for specific cases. They are nonetheless interesting as they reveal the influence of certain factors or parameters on the processes.

This leads to very useful dimensionless numbers. These analytical solutions and the dimensionless equations are presented and used in these volumes. For the numerical methods of the solution of equation systems, the reader is referred to specialized publications.

The subject of extractive metallurgy is also addressed in two other publications written by myself. The first volume, *Basic Thermodynamics and Kinetics*, deals with the fundamentals of thermodynamics and kinetics of the extraction processes. This second volume, *Metallurgical Reaction Processes*, deals with the extraction and refining unit processes. The third volume, *Processing Operations and Routes*, deals with the operations and technologies used in industrial production and industrial processing routes, i.e. the combination of steps or operations used to convert the available ore to metal, illustrated by flowsheets.

This book is intended not only for students of metallurgical and mechanical engineering who want to acquire the bases of this technology, decreasingly taught in universities and engineering schools, but also for engineers confronted with a new production problem, either directly (management of a industrial operation or development of a new process) or indirectly (in the definition of a materials' specification).

It is conceived to be accessible to any student or engineer with general chemistry and physics training. It only necessitates elementary knowledge in chemistry, thermodynamics and chemical kinetics. One of the objectives of this book is to allow the easy consultation of books and technical publications dealing with this field.

This book is the result of my chemical engineering training, courses taught in the Écoles des Mines of Nancy and Paris (France), visits to industrial plants, research performed in collaboration with industry, studies and common work as a consultant and as an industrialist in direct contact with numerous producers of metallic parts. I

would like to thank, more particularly, engineers from the research centers of Arcelor-Mittal (IRSID), Alcan (ex-Péchiney), Cezus and Eramet for their advice and authorized opinions.

I would most particularly like to thank Professors Jean Philibert and André Pineau. Finally this book is dedicated to Professors Pierre Le Goff and Pierre-Marie Fourt.

Alain VIGNES  
February 2011

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[1](#) S.L. SASS, *The Substance of Civilization: Materials and Human History from the Stone Age to the Age of Silicon*, Arcade Publishing, 1999.

[2](#) J.P. MOHEN, *Métallurgie préhistorique*, Masson, Paris, 1990.

[3](#) US Geological Survey, *Minerals Commodity Summaries and Minerals Yearbook*, 2007.

[4](#) Source: IISI (International Iron and Steel Institute).

[5](#) J. SZEKELY, "The mathematical modeling revolution in extractive metallurgy", *Metallurgical Transactions B*, Vol. 19B, p. 525-540, 1988, and H.Y. SOHN, "The coming-of-age of process engineering in extractive metallurgy", *Metallurgical Transactions B*, Vol. 22B, p. 737-754, 1991.

# Chapter 1

## Hydrometallurgical Extraction Processes

### 1.1. Overview of hydrometallurgical processes

Hydrometallurgical processing routes of ores, concentrates, residues and wastes consists of a sequence (or combination) of unit operations where physical or chemical unit processes are performed:

- physical processes, called *separation processes*, include: flotation, filtration and distillation (these are studied in [VIG 11c], [Chapter 1](#));
- chemical processes include: leaching (dissolution), precipitation and solvent extraction (SX);
- electrochemical processes include: *electrowinning* of an electrolytic purified solution in order to obtain the pure metal; *electro-dissolution* of mattes; and electro-dissolution of impure metals (*electrorefining*) (these processes are studied in [Chapter 2](#)).

The sequence of leaching, separation (by precipitation or solvent extraction) and/or electrometallurgy is general.

This chapter deals with the extraction processes that occur in hydrometallurgical unit operations and with the

hydrometallurgical processing routes (illustrated by flow sheets) of oxide ores, sulfide concentrates and mattes.

The leaching operation of an ore or concentrate with an aqueous lixiviant solution is widely used in metal recovery from ores or concentrates, since many oxides or sulfides form soluble salts in aqueous media. It produces partial or complete dissolution of the components of an ore/concentrate in the aqueous solution. In the

case of partial dissolution, a filtration or decantation of the solid residue allows the dissolved components to be separated from the non-dissolved. In the case of components' total dissolution, the separation of the leaching products will then be performed, either by solvent extraction or by selective precipitation. In some operations, dissolution of a constituent (component) occurs simultaneously with the precipitation of another component. This operation will then be followed by filtration of the precipitate.

The hydrometallurgical processing routes of the ores or of the concentrates of the main metals are presented as flow sheets in [section 1.5](#).

These processes occur by homogeneous or heterogeneous reactions involving ions, either as reactants or products, with or without electrical charge transfer. These reactions are of three types:

- *acid-base reactions* without any electrical charge transfer, see [VIG 11a], [Chapter 5, section 5.4.4](#);

- *redox electrochemical reactions*, occurring by an electrochemical process, see [VIG 11a], Chapter 8, section 8.5; or

- *complexation reaction*, simple or coupled with redox reactions, see [VIG 11a], [Chapter 4, section 4.2.3](#).

The operating conditions of the dissolution or precipitation of a metal, oxide or sulfide are gathered in the Pourbaix



diagrams, see [VIG 11a], Chapter 8, section 8.3. The Pourbaix diagram is the basic tool of hydrometallurgical processing operations.

## **1.2. Leaching processes**

### **1.2.1. *Basic features***

Leaching industrial operations are carried out on oxidized ores, oxide mixtures (slags, etc.), sulfide ores or concentrates obtained by flotation, mattes from conversion operations and ores containing precious metals in their native state in order to extract these metals.

#### **1.2.1.1. *The leaching chemical reactions***

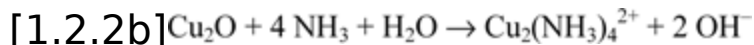
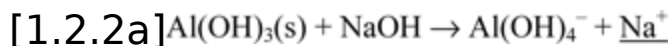
Leaching can be obtained by different types of reactions:

- Leaching of oxides by acid or alkaline reactions:

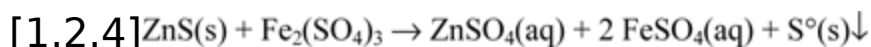
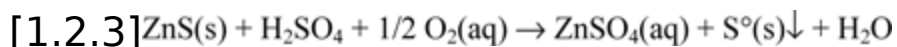
- acidic (sulfuric or hydrochloric) leaching:



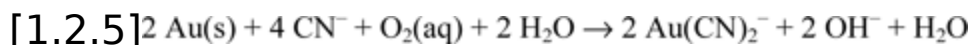
- basic (caustic soda or ammonia) leaching with formation of complexes:

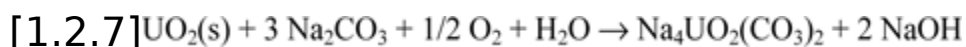
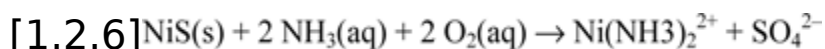


- oxidative leaching of sulfides by redox electrochemical reactions:

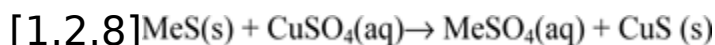


- oxidative leaching of metals, sulfides and some oxides with formation of complexes:

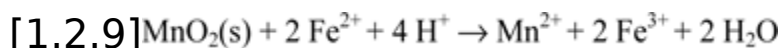




– Leaching by metathetic reactions (see [VIG 11a], Chapter 8, section 8.5.1):

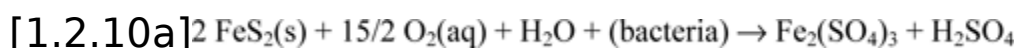


– Reductive leaching reactions:

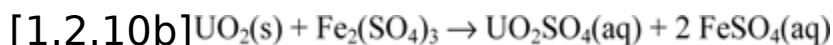
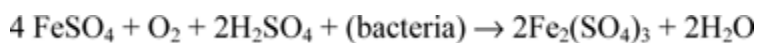


– Microbiological or bacterial leaching reactions:

– direct:



– indirect:



The action of bacteria on redox chemical reactions has been known for a long time. These micro-organisms catalyze chemical reactions that are extremely slow at room temperature. In this book, bio-hydrometallurgy is not presented. Detailed studies can be found in [BIO 03, BRI 01, HER 01, MOR 01].

### **1.2.1.2. *Leaching solution chemistry, operating parameters and operations***

Leaching of oxidized ores and sulfide ores depends on numerous parameters. An inherent feature of the processing of minerals is the fact that every ore is different. Leaching operations cannot be designed without laboratory and pilot testing of the ore or concentrate of interest.

The acid lixiviants of industrial leaching are mainly sulfuric acid and chlorhydric acid. The advantages and drawbacks of these acids are presented in [Table 1.2.1](#). The alkaline lixiviants are caustic soda (NaOH), sodium bicarbonate ( $\text{CO}_3\text{Na}_2$ ), ammonia ( $\text{NH}_3$ ) and sodium cyanide (CNaNa).

Sulfuric acid does not attack silica gangues; however, it dissolves carbonated gangues. Carbonated gangues are not dissolved by caustic soda. Sodium bicarbonate ( $\text{NaHCO}_3$ ) or ammonium carbonate  $(\text{NH}_4)_2\text{CO}_3$  are used as leaching reagents to attack ores with limestone or magnesia gangues (see reaction [1.2.7]). Ammonia can also be used, see reactions [1.5.11] and [1.5.12]. Such reactions are carried out on uranium and copper oxides when attack of the gangue-containing limestone or dolomite (oxides, sulfates or carbonates) may consume too much sulfuric acid.

**Table 1.2.1.** *Specific characteristics of sulfuric and hydrochloric acids for leaching processes*

<i>Sulfuric acid</i>	<i>Hydrochloric acid</i>
Natural lixiviant of sulfides	Strong lixiviant. Proton activity increases with higher $[\text{Cl}^-]$ content
Very low vapor pressure	High vapor pressure requires closed equipment
Sulfate ions can easily be removed from solution by precipitation	Metal separation from solution by solvent extraction (SX) is facilitated by the formation of ionic complexes of different stability
Acid modestly corrosive for reactor materials	Very corrosive acid
Electrowinning of numerous metals in sulfate solutions is performed owing to the formation of oxygen gas	Electrowinning of metals in chloride solutions is not used industrially and yields chlorocomplexes (see [VIG 11a], Chapter 8, section 8.2.2.3) and release of chlorine gas

Temperature, pH and oxidative potential are the operating parameters of leaching operations. Leaching operations are performed at atmospheric pressure at  $T < 100^\circ\text{C}$  or at a temperature up to  $250\text{--}270^\circ\text{C}$ . The pressure within the reactor has to be higher than the vapor pressure of water, which reaches 40 atm (4,000 kPa) at  $250^\circ\text{C}$ .

as the oxidation potential is usually fixed ( $P_{\text{O}_2}$  or  $[\text{Fe}^{3+}]/[\text{Fe}^{2+}]$ ), the leaching progress will depend on the evolution of acidity (or basicity) of the solution used during the operation.

These leaching operations are carried out in reactors with several compartments (see [VIG 11c], [Chapter 2](#), section

2.1.1) working with a continuous feed of the leaching solution and particles, the pulp circulating from one compartment to another. Therefore, the composition of the attack solution, especially its pH, varies from the first compartment to the last, as the acid is consumed or produced along the reactor. This explains the fact that different reactions can occur between the first and last compartment; for instance, dissolution then precipitation of iron oxide. When an oxidizing gas is used, the injection is performed in each compartment. Regeneration of the primary oxidizing reactant ( $\text{Fe}^{3+}$ , for instance) is then effective throughout the reactor. The oxidizing capacity is therefore kept but the acidity of the leaching solution varies along the reactor.

## ***1.2.2. Leaching of oxides with acid-base reactions***

### **1.2.2.1. Basic features**

Oxides or oxidized ores that are attacked in industrial leaching (digestion) operations are:

- aluminum oxide ores (bauxite), see [section 1.5.1](#);
- the products of the calcination of sulfide zinc ores, see [section 1.5.2](#);
- oxidized copper ores (malachite), see [section 1.5.3](#);
- laterites, see [section 1.5.4](#);
- uranium oxide ores, see reaction [[1.2.10b](#)]; and
- ilmenite ores.

Most of these ores contain iron oxides, which are a by-product. Depending on the ore and its content in iron oxide, the leaching reaction will be a selective dissolution of the desired oxide, a total dissolution of the ore oxides or a leachingprecipitation (dissolution of every oxide, followed in

the same reactor by precipitation of the iron oxide). The precipitation of iron oxides or hydroxides is studied in [section 1.3.1.3.1](#). The pregnant leach solution (liquor) undergoes a subsequent separation operation.

The thermodynamic data on the solubility of oxides and hydroxides (see [VIG 11a], [Chapter 4, section 4.2.4](#)) set the basic operating conditions of a leaching operation, especially the type of reagent (acid or alkaline) and pH of the solution. They are featured on the corresponding Pourbaix diagram, see [VIG 11a], Chapter 8, section 8.3. For instance, the Pourbaix diagrams of the Al-H<sub>2</sub>O and Fe-H<sub>2</sub>O systems (see Figures 8.3.5 and 8.3.3) show that alumina starts to dissolve in an alkaline solution at pH 8, whereas iron oxide only starts to dissolve at pH 13 (at 25°C). This explains the leaching/digestion of bauxite with sodium hydroxide. For zinc ores rich in iron oxide, acidic leaching dissolves both iron and zinc oxides, whereas alkaline leaching only dissolves zinc oxide.

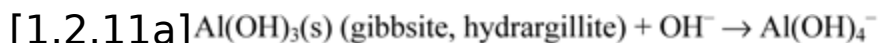
The leaching solution will be acid or alkaline depending on whether we want total dissolution of the oxides (including iron oxide) or selective dissolution of the desired oxide.

The kinetics (effect of the nature and content of the acid or base) of these acidbase reactions are presented in [VIG 11a], [Chapter 5, section 5.4.4](#). Many other parameters or factors have a strong effect on the leaching rate. In an acidic and in an alkaline medium, the dissolution rate of a hydroxide is usually much faster than the dissolution rate of the corresponding oxide. Under the same conditions, dissolution of the amorphous ferric hydroxide Fe(OH)<sub>3</sub> is at least 10 times faster than dissolution of goethite α-FeOOH. The dissolutions of nickel hydroxides Ni(OH)<sub>2</sub> and Ni(OH)<sub>3</sub> at 50°C in an acidic solution (0.01 mol/L SO<sub>4</sub>H<sub>2</sub>) and in an ammoniacal solution (1 mol/L NH<sub>4</sub>OH) are extremely rapid, whereas the dissolution of oxide NiO is quite slow.

The main factors, besides temperature, influencing the dissolution kinetics of oxide particles are its oxidation state, its crystalline (and grain size) or amorphous state. In addition, in an acidic medium the factors are the activity of H<sup>+</sup> ions and the nature and content of the anion(s) present that control the formation of complexes. In an alkaline medium, the factors are the pH and the reducing or oxidizing conditions.

### **1.2.2.2. *Leaching of aluminum oxides and hydroxides***

The leaching (called digestion) of bauxite alumina hydroxides and oxides is industrially performed with caustic solutions (see [section 1.5.1](#)):

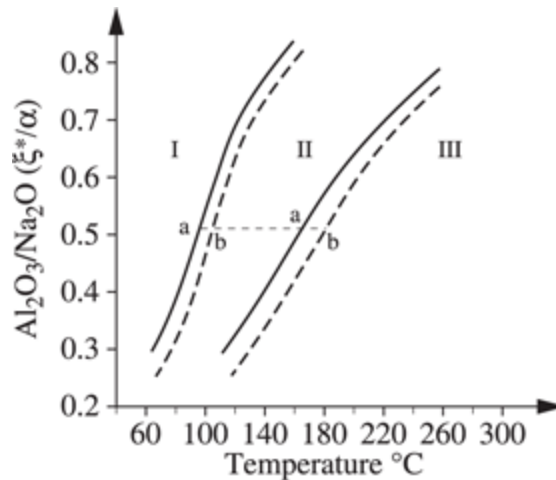


The  $\xi^*/\alpha$  ratio variations – where  $\xi^*$  is the dissolution degree (see equation [\[1.2.5\]](#)) that would be reached at equilibrium and where  $\alpha$  is the molar concentration of Na<sub>2</sub>O in the leaching solution – as a function of temperature for the oxides are shown in [Figure 1.2.1](#).

A relatively low NaOH concentration (1.2 mol/L) and temperature of 140–160°C allow an almost complete dissolution of 1 mol/L of gibbsite Al(OH)<sub>3</sub>(s). For boehmite  $\gamma$ -AlOOH, a temperature of 230°C has to be reached for total dissolution. The solubility curves of boehmite as a function of pH and temperature are shown in Figure 4.2.11 [VIG 11a]. For  $\alpha$ -AlOOH diaspor, higher temperatures are required [AUT 01].

In the industrial operations of bauxite digestion, the operating conditions are imposed by the dissolution-precipitation of the silicates of the ore, see [section 1.5.1](#), reaction [\[1.5.3\]](#).

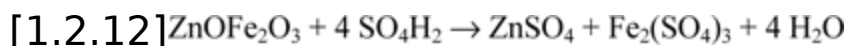
**Figure 1.2.1.** *Leaching of alumina. Solubility curves (in terms of the ratio  $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ ) for gibbsite and boehmite as a function of temperature, at two caustic concentrations: (a) 2.36 molar  $\text{Na}_2\text{O}$ ; (b) 1.42 molar  $\text{Na}_2\text{O}$ , stable phases; (I) gibbsite ( $\text{Al}(\text{OH})_3$ ); (II) boehmite  $\gamma\text{-AlOOH}$ ; (III) diaspor  $\alpha\text{-AlOOH}$  [BAR 64]*



The leaching of alumina  $\text{Al}_2\text{O}_3$  in sulfuric acid solutions is very slow for concentrations of acid ranging from 30–40% at  $100^\circ\text{C}$ . Thirty per cent of alumina is dissolved after 16 hours at  $108^\circ\text{C}$ . Concentrated sulfuric acid (96%) has to be used at  $100^\circ\text{C}$  to obtain total dissolution of  $\text{Al}_2\text{O}_3$ .

### **1.2.2.3. Leaching of ZnO oxide and of ferrite $\text{ZnOFe}_2\text{O}_3$**

The dissolution of zinc oxide ( $\text{ZnO}$ ) at low temperature in an acidic medium (pH 1.7) is complete and fast (see reaction [1.2.1]). The completed dissolution of ferrite  $\text{ZnOFe}_2\text{O}_3$  is achieved in a strongly acidic medium (hydrochloric and sulfuric acid) with the formation of zinc sulfate and ferric sulfate:



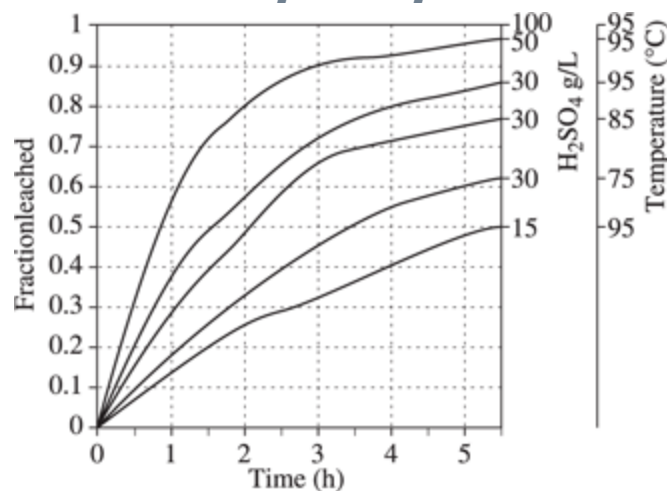
This reaction is relatively slow. It depends on the temperature and sulfuric acid concentration, see [Figure](#)



[1.2.2.](#) For particles of 20  $\mu\text{m}$  and a sulfuric solution with a concentration of 1 M at 95°C, more than 90 minutes are necessary to obtain complete dissolution (kinetic data on these reactions are presented in [VIG 11a], [Chapter 7](#), sections 7.2.1.3 and 7.2.2.3.1 and Figure 7.2.3).

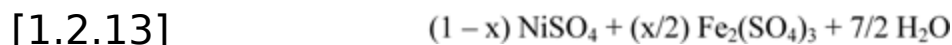
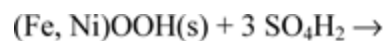
The separation of zinc from iron is then performed by precipitation of iron oxide, see [section 1.5.2.1.2](#).

**Figure 1.2.2.** *Leaching of zinc ferrite  $\text{ZnOFe}_2\text{O}_3$  with sulfuric acid (reaction [1.1.2]) – effects of temperature and sulfuric acid concentration [FIL 92]*



### 1.2.2.4. **Leaching of laterites (nickel oxide ores)**

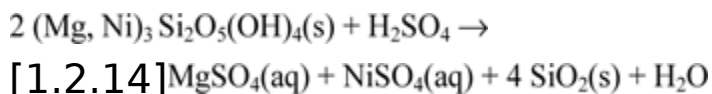
Limonitic laterites are mainly  $\alpha$ -goethite ( $\text{FeOOH}$ ) containing 0.8–1.8% Ni, 50–75%  $\text{Fe}_2\text{O}_3$ , 0.5–5% MgO and 1.5–6%  $\text{SiO}_2$ . The leaching, with concentrated sulfuric acid solutions, between 95 and 105°C, dissolves goethite as sulfates:



For a suspension of porous goethite particles, with an average size of 6.55  $\mu\text{m}$ , in water (20% in mass) and an initial  $\text{H}_2\text{SO}_4$  concentration of 270 g/l (acid/dry ore weight

ratio 1:4), the dissolution is complete in two hours. The final concentration in H<sub>2</sub>SO<sub>4</sub> ranges from 20–25 g/l and the concentration in Fe (III) is in the order of 80 g/l.

For saprolitic laterites (Ni 1–3.5%, Fe<sub>2</sub>O<sub>3</sub> 10–30%, MgO 25–38% and SiO<sub>2</sub> 40–55%), the main component is a magnesium/nickel silicate whose leaching yields magnesium and nickel sulfates:



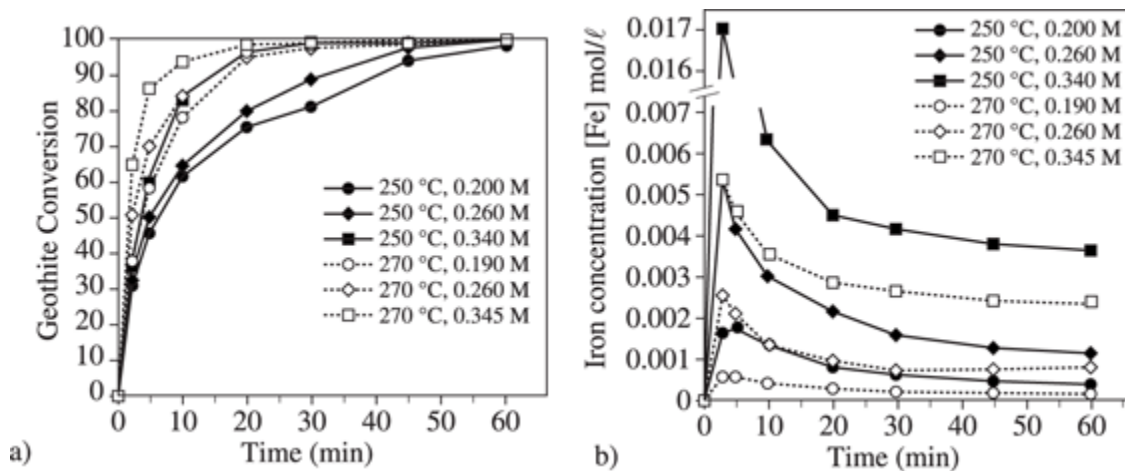
With particles of 20 µm and a pulp made of 20% solid and a 260 g/l sulfuric acid solution at 98°C, the fractional extraction of nickel is 96% in one hour at 98°C [CUR 04].

The leaching of limonitic laterites consumes a small amount of sulfuric acid. The leaching of saprolitic laterite, owing to the presence of significant amount of magnesia, consumes much more.

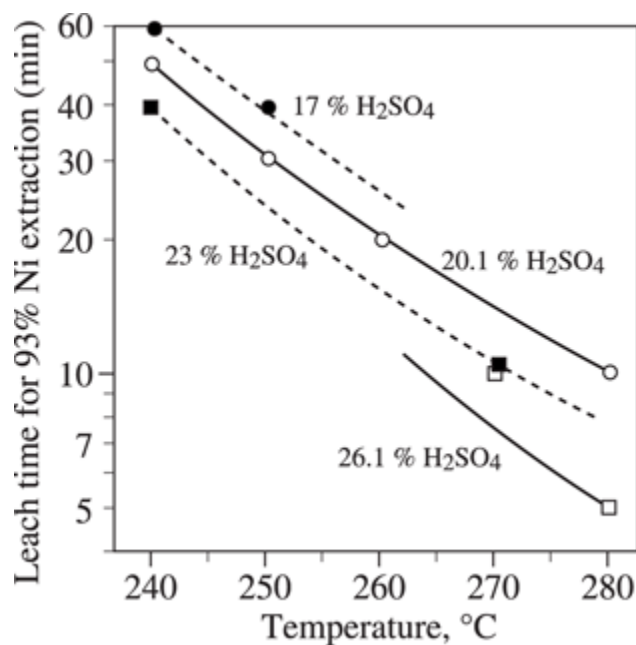
Industrially, these saprolitic laterites are mainly treated using pyrometallurgical processes.

The industrial leaching process of limonitic laterites is the “PAL” process, under pressure (from 36–55 atm) at high temperature (250–280°C), see [Figure 1.5.6](#). The leaching is performed with diluted sulfuric acid solutions from 0.20–0.40 mol/L and with acid/dry ore weight ratios ranging from 0.2–0.5:1. For micron size (1–3 µm) porous particles (65 m<sup>2</sup>/g) there is no dissolution at 220°C. Dissolution starts above 240°C and is total in 20 minutes at 270°C, see [Figure 1.2.3a](#). It increases with sulfuric acid content, see [Figure 1.2.4](#). As the acidity decreases with leaching progress, precipitation of the dissolved iron as hematite occurs in the last compartment of the autoclave (see [Figure 1.2.3b](#), [sections 1.3.1.3](#) and [1.2.1.2](#) and [VIG 11c], [Chapter 2](#), [Figure 2.1.2](#)).

**Figure 1.2.3.** *Leaching/precipitation of limonitic laterites with sulfuric acid at high temperature and final concentration of  $\text{SO}_4\text{H}_2$ : a) kinetics of goethite dissolution (22% solids, 2.42 mol/L  $\text{FeOOH}$ ); and b) concentration of dissolved iron as a function of leaching time. The precipitation process is controlled by the kinetics of dissolution. During the operation, the concentration of  $\text{SO}_4\text{H}_2$  decreases by consumption, then increases owing to the precipitation of  $\text{Fe}_2\text{O}_3$ , see reaction [1.3.7] [PAP 96]*



**Figure 1.2.4.** *Leaching of limonitic laterite particles – the effects of temperature and acid concentration on leach time for 93% nickel extraction. Initial parameters: 20% solids, 0.5 M  $\text{SO}_4\text{H}_2$  [BER 99a]*

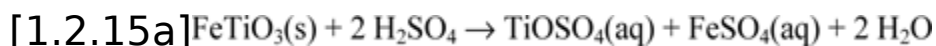


### 1.2.2.5. *Ilmenite leaching*

The enrichment in titanium oxide (TiO<sub>2</sub>) of ilmenite (FeTiO<sub>3</sub>) for pigment production [ZIE 04] by selective dissolution of iron oxide is industrially performed by leaching ilmenite with sulfuric or hydrochloric solutions.

With a dilute sulfuric solution (22–23%), after eight hours at 130°C a solid residue is obtained, with a composition of 97% TiO<sub>2</sub>, 1% Fe<sub>2</sub>O<sub>3</sub>, 0.5% Al<sub>2</sub>O<sub>3</sub> and 0.5% SiO<sub>2</sub>.

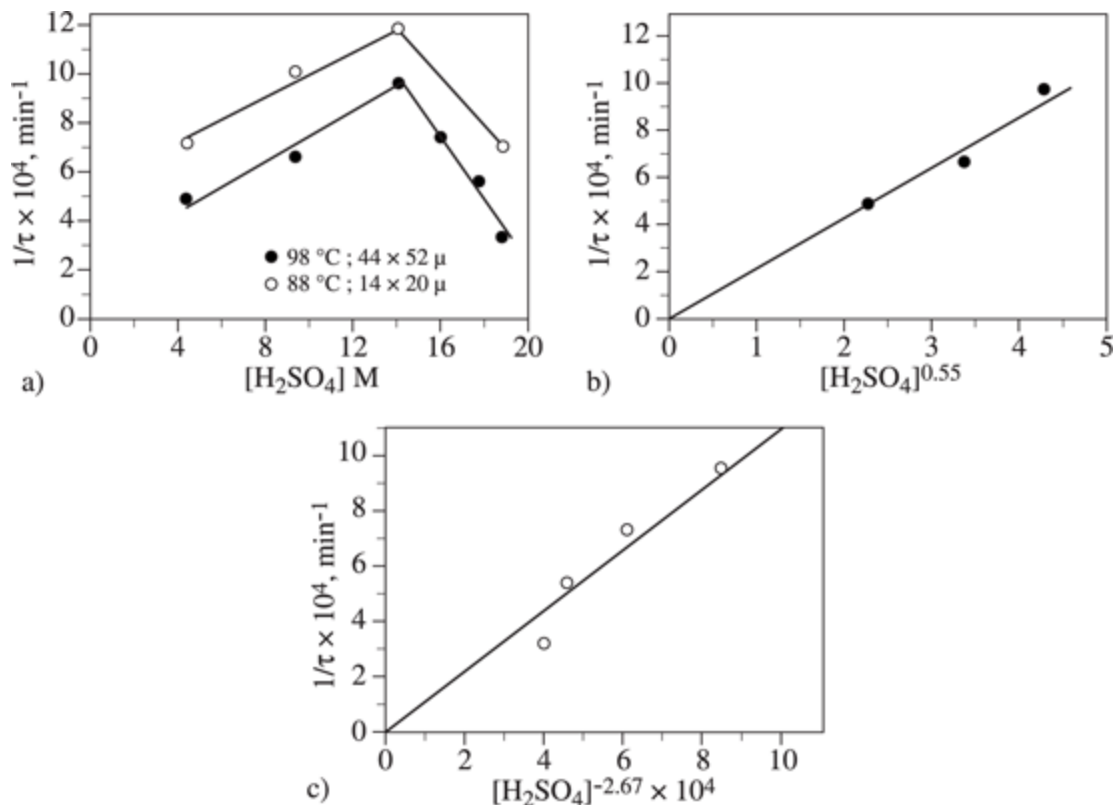
At around 100°C, with concentrated sulfuric solutions (from 4 to 12 M), dissolution of an ilmenite FeTiO<sub>3</sub> particle occurs under chemical reaction control (see equation [7.2.7]). The constant  $k_B$  of the particle fractional conversion kinetic law (see [VIG 11a], [Chapter 7](#), equations [7.2.7]) depends on the H<sub>2</sub>SO<sub>4</sub> concentration with an order of 0.55 (see [Figure 1.2.5b](#)):



For even more concentrated solutions (>16 M), the constant  $k_B$  of the particle fractional conversion kinetic law significantly decreases with an order of -2.5 with respect to

sulfuric acid concentration  $[\text{H}_2\text{SO}_4]^{-2.57}$  (see [Figure 1.2.5c](#)) owing to the formation of solid sulfate layers:  $\text{TiOSO}_4(\text{s})$  and  $\text{FeSO}_4(\text{s})$  around the particles.

**Figure 1.2.5.** *Leaching of ilmenite in sulfuric acid solutions: a) effect of  $\text{H}_2\text{SO}_4$  concentration on the constant  $k_B = k^1$  of the particle fractional kinetic law at 98°C; b) plot of  $(1/\tau)$  versus  $[\text{H}_2\text{SO}_4]^{0.55}$  for  $[\text{H}_2\text{SO}_4] < 12\text{M}$ ; and c) plot of  $(1/\tau)$  versus  $[\text{H}_2\text{SO}_4]^{-2.67}$  for  $[\text{H}_2\text{SO}_4] > 12\text{M}$  [HAN 87]*



### 1.2.2.5.1. Sulfate process

In the industrial “sulfate” process, leaching is performed with 98.5% sulfuric acid. The exothermic reaction [1.2.15] is initiated by steam heating and the temperature reaches 170–220°C. The operation time is 10–12 hours. The reactions generate significant release of steam. A solid mass