ACID AND THERMAL TREATMENTS OF LATERITIC BAUXITES

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Abstract

H_2SO_4 and HCl processes accompanied by thermal treatments at different stages are described for the industrial extraction of alumina from lateritic clay minerals, especially from kaolinite, an important component of lateritic bauxites. The effects of calcination at high temperatures on the pretreatments of the raw lateritic materials, as well as on the thermal transformations of the products (salts) resulting from the acid treatments of lateritic bauxites are analyzed. Beside energetic considerations, separation methods of Al from Fe and from other lateritic-metallic components are emphasized in the extraction and purification processes.

The mechanism of a controlled HCl-extracting treatment performed on iron-bearing kaolinite is described, as well as its characterization by IR and DTA ad hoc methods, enabling to distinguish between Al and Fe in the structure of lateritic kaolinite. The location and quantification of Al in the structure of lateritic goethite is also considered.

Keywords: acid and thermal treatments, alumina, DTA, IR, lateritic bauxites, location of Al and Fe in lateritic kaolinite and goethite

Introduction

Acid treatments have been employed for the extraction of alumina from non-bauxitic raw materials and from silica-rich bauxitic or lateritic ores. In the latter case the extraction of alumina and other metal oxides may be deemed selective if silica is not dissolved by the mineral acids used in such treatments.

Usually, the above mentioned acid processes need a thermal input in order to speed up and achieve a final degree of extraction. Various aluminium salts are produced in the acid processes. Alumina (α-Al_2O_3) is obtained by the decomposition and calcination of these salts, eventually enabling the regeneration of the acids. The purity and physical structure of the alumina produced by the acid processes differs substantially from that obtained by the Bayer alkaline process. On the other hand the reactivity of some products resulting from the acid and thermal treatments of lateritic

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bauxites may be substantially enhanced. The kind of ore and energetic sources available, beside other economic factors are to be considered in order to choose the appropriate alumina extraction process.

Acid and thermal treatments (including differential thermal analytical methods) of lateritic bauxites and related synthetic and raw minerals from many countries have been described [1–9]. Some of these processes will be mentioned in this contribution. The results of these processes are related to the composition, mineralogy and location of each ore. Beside the above mentioned processes, in this contribution I shall mostly refer to the acid treatments of lateritic bauxites located in the region 'Los Guaicas', Bolivar state (south of Venezuela), henceforth named 'LG' laterites.

Acid treatments

Sulfuric acid

The extraction of alumina from clay minerals, mostly by sulfuric and hydrochloric acids, has been exploited by many countries during World War II. Grim [10] describes many extraction processes, some of them being discussed here. The acid dissolution varies with the nature of the clay and the kind of acid, the acid concentration, the acid-to-clay-ratio, the temperature and duration of treatment [11]. Generally, the degree of crystallinity of a particular clay also determines the solubility, as is the case of kaolinite, whose solubility increases as the crystallinity decreases. Grinding the clay minerals – which has also an effect on its particle size – influences as well their solubility in acids. Mechanochemical reactions – which cause also selective structural transformations, including irreversible amorphization – may result from the grinding process of different clay minerals [12]. In contrast, controlled heating (in air) of clay minerals leads to transformations into disordered structures and recrystallization into new phases at high temperatures. In the application of each one of these solid-state pretreatments for increasing the solubility of the raw materials, the energy consumption must be considered.

Calcining the clay minerals also changes their solubility characteristics. Depending on the temperature and the structure of the clay, calcining may enhance or reduce solubility in a particular acid. Pask and Davies [13] have shown, using 0.5 g of clay dried at 130°C in 30 cm^3 of sulfuric acid (20%) and boiling for one hour, that only about 3% of total alumina was dissolved from kaolinite, whereas under the same conditions, 50–90% alumina was dissolved from halloysite, which has a related structure to kaolinite. However the solubility of montmorillonite – which has a three-sheet structure – ranged from 33 to 87% of total alumina. Keeping the same treatment conditions but after heating the clays at 800°C, practically all of the alumina from both kaolinite and halloysite was dissolved, whereas the solubility of montmorillonite in sulfuric acid actually decreased. It is well known that at 800°C the structures of both kaolinite and halloysite become quite disrupted and are transformed into metakaolinite and metahalloysite, respectively. Both these products are amorphous, hence more susceptible to be attacked by the acids. In the case of mont-

morillonite, upon heating at 800°C the structure has been changed but not substantially disrupted; hence alumina cannot be thoroughly extracted. Some montmorillonite clays may be activated by controlled acid and thermal processes. By varying the treatment procedure it is possible to produce a variety of activated products which have specific advantages for particular processes and oils [10]. Depending on the conditions of the acid process, the resulting montmorillonite products may have decolorizing or catalytic properties. As well, acid activation processes cause an increase of the surface area and pore size distribution in the catalysts obtained from iron-free kaolins.

When kaolinite (and some other clay minerals) are heated to higher temperatures (~975°C) new crystalline phases develop, hence the solubility of the alumina decreases. The high temperature forming-phases vary with isomorphic substitutions in the minerals structures, as has been shown by Yariv *et al*. on the interactions between Fe and Al during the heating of lateritic bauxites [14]; thus correlative variations of solubility in acid would be expected. With acids of the same concentration and similar acid-to-clay-ratio but with digestion under pressure at 155°C, the solubility of all the clays increased [13]. Anyway, the degree of alumina extraction with concentrated sulfuric acid is quite high, even in the absence of the thermal pretreatment of kaolin clays submitted to the acid leaching process. In addition to kaolinite, when other kind of clays are attacked by sulfuric acid the degree of Al extraction is quite high as well. This was shown for instance in a study of the kinetic parameters derived from the leaching by sulfuric acid of a complex raw material containing kaolinite, illite and mixed layer clays [15]. Beside the acid concentration and reaction temperature established during the leaching process, pretreatment activation conditions of the raw material (calcinations temperatures and time-controlled grinding) ruled the kinetics of this reaction.

The main salts resulting from the sulfuric acid leaching process of lateritic clays are aluminium sulfates with different degrees of crystallization water. As iron and aluminium have close thermodynamic constants it is difficult to separate these two elements when they are present together. Thus, the removal of iron – which is abundant in bauxitic laterites – from sulfuric acid leach liquors is a special problem. In a chapter on the development of acid processes for alumina production, Ziegenbalg [16] described purification methods that can be achieved by repeated crystallization and precipitation of alkali alum or basic aluminium sulfate, the iron being concentrated in the acid leaching liquor. In order to prevent the formation of mixed crystals, Fe^{3+} is generally reduced to Fe^{2+} prior to the deposition of the aluminium compound.

Another preliminary method of separation of iron from aluminium by a hot sulfuric acid treatment of kaolinite contained in 'LG' laterites, consisted in selective dissolution and precipitation techniques of the resulting sulfate salts in some organic solvents [17]. The purified aluminium sulfates (mostly $Al_2(SO_4)_3 \cdot 6H_2O$) upon decomposition and calcination were converted to a high grade α alumina.

On a pilot scale basis of the acid processes, the purification and separation of Al-salts as well as the acid recovery are important factors to consider. Moreover, the decomposition of aluminium sulfate requires high energy consumption.

Hydrochloric acid

The solubility of clay minerals in other acids has been also explored. The extraction of alumina from kaolinite by HCl depends mostly on the acid concentration and reaction temperature. A first order degree and an activation energy of about 20 kcal mol^{-1} has been reported for this reaction [18]. Aluminium which substitutes partially silicon in the tetrahedral layer is more difficult to remove than Al located in the octahedral layer. Magnesium and iron which are abundant in the structure of other clay minerals, are easily extracted by HCl. On the other hand, the solubility is likely to be considerable for acids with an anion having a size and geometry approximating that of the component part of the clay minerals structure. Therefore some relatively weak acids may strongly attack certain clay minerals. Murray [19] has shown, i.e. that phosphoric acid attacks kaolinite under some conditions more strongly than sulfuric acid does, in spite that sulfuric acid is a stronger acid than phosphoric acid.

Ziegenbalg [16] has also described the development of acid processes for alumina production from silica-rich materials. Thus, when aluminosilicates are treated with HCl, the formation of gelatinous SiO_2 residues are observed, but they can be handled in the solid–liquid separation. In this work have been discussed also acid-leaching treatments that have been employed for the extraction of alumina from bauxitic minerals, as an alternative to the Bayer process (alkaline digestion). This publication [16] reports many acid processes, the most important being a Hungarian process of a SiO_2-rich bauxite leached with HCl, followed by ion exchange for the iron recovery. $AlCl_3·6H_2O$ is the main product resulting from this process. Subsequently, there are many steps for the separation and purification of this salt followed by its thermal decomposition, in order to produce alumina of the required properties and to enable the acid regeneration. Favorable conditions exist for the thermal decomposition of the above mentioned aluminium chloride, since the HCl emitted and separated in this thermal reaction is not decomposed, hence it may be isothermally or adiabatically absorbed by conventional methods to yield HCl of various concentrations. In the HCl as in other acid processes, however, comparative energetic considerations and other variables must be accounted for, including the yield and quality of the alumina product. An important step in the acid processes is the removal of impurities like Na, K, Ca, Mg, etc., originally present in the raw material. A process which reported the heating of iron-rich bauxites with ammonium chloride, achieved a major removal of iron from these bauxites [20]. As well, some selective processes for the removal of iron from bauxites by hydrochloric acid have been mentioned [e.g.21].

Characterization and extraction of lateritic minerals

As kaolinite is an important component of laterites, this section will show the use of HCl and other extraction treatments as well as spectroscopic and thermal methods for discerning the location of iron in the structure of lateritic kaolinites. Moreover, the location of Al in the structure of lateritic goethite will be also considered.

Table 1 which is partly reproduced from the studies of Mendelovici *et al*. on the heating of lateritic bauxites [22], displays the mineralogical composition of four representative lateritic samples taken from an 11 m thick section ('LG' laterites location). Two samples were chosen for this investigation, one containing ~80% kaolinite (sample a) and the other containing ~40% kaolinite and ~40% gibbsite (sample b). These two samples contain different amounts of goethite. It was established that isomorphic substitution of Fe by Al takes place in these lateritic goethites [23]. Between 11 and 24% was the Al substitution range determined in the mentioned lateritic goethites.

Table 1 Content of minerals in the laterite samples used in this study

Minerals	Laterite composition/%			
	'a'	'b'	'c'	'd'
Quartz[*]	10	6	9	Trace
Kaolinite[*]	80	40	5	5
Kaolinite[**]	70	47	10	11
Gibbsite[*]	Trace	40	70	70
Gibbsite[**]	Trace	10	48	51
Gibbsite[***]	Trace	16	44	52
Goethite[+]	11	22	22	26
Ilmenite[**]	7	7	8	13

[*]Approximate estimation by XRD and/or IR.
[**]Approximate estimation from total chemical analysis of the elements (kaolinite, calculated from total SiO_2 minus quartz SiO_2; gibbsite calculated from total Al_2O_3 minus kaolinite Al_2O_3; ilmenite calculated from total TiO_2).
[***]Estimated by selective consecutive dissolutions with boiling 0.5 M NaOH.
[+]Estimated by the modified CDB treatment.

These samples were submitted to the following selective chemical dissolution methods: goethite was extracted by an exhaustive citrate–dithionite–bicarbonate (CDB) method, as the substitution of Al affects the solubility of goethite. After this first treatment, namely a complete dithionite extraction of free iron oxides, the samples still contained relatively high amounts of iron presumably incorporated in the aluminosilicate and ilmenite phases (Table 1). Citing some sections from another contribution published on the same laterite materials [24] I shall describe and discuss here the following experimental treatments which are relevant for this work: gibbsite was removed from the CDB deferrated (iron-free) samples by shaking with 1.25 M NaOH at 75°C. Structural iron and aluminium were extracted from the gibbsite-free kaolinites after shaking each sample with 1.0 M HCl at 40°C. For each sample 23 consecutive extractions over 24 or 72 h periods were performed. After each extraction and decantation iron and aluminium were determined in the supernatant by atomic absorption spectrometry. The separated solids were washed with water and dried with acetone for a comparative infrared (IR) spectroscopic investigation. CsCl, KI and KBr were selec-

tively used as matrixes for the preparation of the IR disks of natural, deferrated and HCl-extracted samples. The CsCl disks were aged at 100°C to allow the formation of a CsCl–kaolinite complex. The CsCl as well as the KI disks were then heated in air at variable temperatures ranging from 200 to 420°C up to 3 days at each temperature. The IR spectral information obtained from the CsCl treatment at 270°C and from the heating at higher temperatures of the KI disks, allowed the location of Fe in the octahedral sheet of lateritic kaolinite (solid solutions of Al and Fe), characterized by absorption bands at 865 and 3607 cm^{-1}, assigned as δAl–OH–Fe and νOH vibrations, respectively. These two frequencies persist after either thermal decomposition or selective chemical dissolution of goethite and of aluminium hydroxide (gibbsite).

In another series of experiments KCl and CsCl mortar-ground mixtures of the same laterite samples containing iron-bearing kaolinite were examined by DTA [25]. In KCl mixtures an endothermic peak at 470–512°C, characteristic of kaolinite, decreased in intensity with increasing iron content in the kaolinite crystal. In CsCl mixtures, such a relationship is obtained only after the removal of gibbsite in the laterite sample. No exothermic peak of kaolinite was detected in the DTA curves of laterites ground either with KCl or with CsCl. In the presence of KCl, the exothermic peak of the lateritic kaolinite overlaps with the endothermic peak of KCl, thus it can not be discerned. When CsCl was employed, as well no exothermic effect was observed in the DTA pattern of standard kaolinite ground with this salt [26].

Thermal reactions of kaolinite with other salts like potassium carbonate have been reported recently [27].

Extraction mechanism of Al and Fe with HCl at 40°C

Figure 1 which is borrowed from the work cited in [24] shows that when the concentration ratios of Al and Fe in the extracting solutions are considered, three stages can be identified in the process. In the first stage which comprises the first four extractions, a high excess of iron is dissolved. This iron originates from the treatment of the CDB
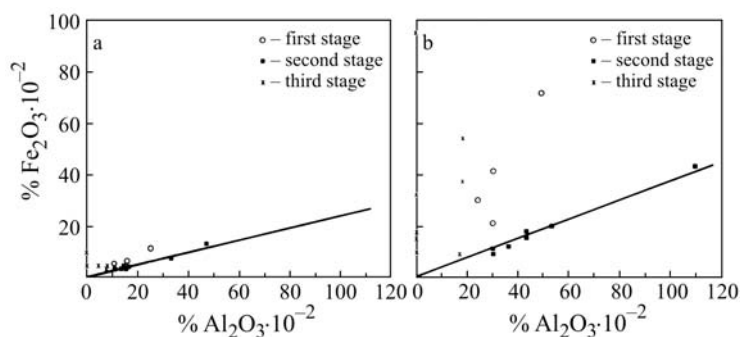
Fig. 1 Percentages of Fe$_2$O$_3$ dissolved from laterites a and b by 1 M HCl *vs.* dissolved Al$_2$O$_3$ (data from Mendelovici *et al.* [24], reproduced with the kind permission of the Mineralogical Society of Great Britain and Ireland)

deferrated laterites with NaOH, in which Al from gibbsite and to some extent Al and Si from kaolinite are dissolved, leaving iron in the solid phase. In the second stage, involving twelve and eight additional extractions for laterites a and b, respectively, a constant ratio between extracted Al and Fe is obtained, which is independent of the acid treatment periods. The linear relationship between the Fe and Al indicates that both elements originate from the same source, namely the octahedral sheet of kaolinite.

In the third stage as the amount of extracted Al sharply decreases, the iron concentration in the extracting solution once more increases. The sharp decrease of HCl-extracted Al in this stage suggests that the surface of the residual kaolinite (the solid remaining from the HCl attack) is coated by the soluble Al and Si species dissolved during the HCl attack. Presumably, this Al and Si species derive in soluble aluminosilicate moieties, which are then adsorbed on the surface of the residual kaolinite forming an amorphous coating. The amorphous surface coatings act as a diffusion barrier in the dissolution process and from this stage on, the dissolution rate depends on the specific diffusion of the elements through these coatings. Thus, the HCl-extraction process above described shows two important aspects: it proves, first of all, the presence of a solid solution of Al and Fe in the octahedral sheet of kaolinite, in agreement with the same conclusions found by the IR spectroscopy studies above explained. Moreover, it explains the different dissolution rates of the elements Fe and Al during the HCl-extraction process.

In this contribution we mention some industrial, acid and thermal processes of lateritic bauxites and related materials leading to the extraction and purification of alumina. In addition, we describe the HCl extraction mechanism of iron-bearing kaolinite as well as adequate IR and DTA methods which are useful for studying the characterization of clay minerals contained in lateritic bauxites.

Such characterization enables to establish i.e. the location of Al and Fe in the structure of both lateritic minerals as kaolinite and goethite. The exact location and content of aluminium in laterites is of considerable importance in predicting whether or not it can be economically extracted from lateritic or bauxitic deposits.

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