

EFFECT OF BAUXITE AND DIGESTION CONDITIONS ON IRON IN SGA

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Abstract

There are many bauxites which, when processed, result in very high iron in solution and consequently product alumina. It is well known that low iron bauxites are more likely to produce high iron in liquor, but that is not always the case. The solubility of iron in liquor from bauxites was studied at varying temperatures and free caustic concentrations. The solubility of iron for iron oxides increases with temperature and free caustic concentration.

Bauxites can contain high levels of a soluble iron species that appears to be present as iron substituted in the gibbsite. On dissolution of that gibbsite the iron is released and, if there is insufficient iron oxide seed present, a high iron in liquor results. The high level of iron within such gibbsites is postulated to occur if there is insufficient iron in the laterisation process for it to precipitate as a separate phase. A soluble iron test has been developed to assist in predicting and controlling iron in product for such bauxites.

1. Introduction

A fundamental premise of the Bayer process is that iron and iron oxides are essentially insoluble in caustic liquors. This enables not only the selective dissolution of the various forms of aluminium hydroxides from an intimate mixture of iron and aluminium hydroxides and oxides, but also enables the use of steel as the main construction material. Under the conditions of the Bayer process steel is essentially in the passive region whereas aluminium and its hydroxides and oxides are highly soluble [1]. Consequently the pregnant liquor contains only trace amounts of iron. On precipitating the aluminium hydroxide from the pregnant liquor virtually all the soluble iron in the liquor is removed and reports to the product alumina. Consequently the product alumina contains only minor levels of iron provided the liquor has been adequately clarified prior to the precipitation step to remove mud particles that can be high in iron content. The iron level of the product required by most alumina customers is less than <0.020% and that can normally be achieved provided good clarities are obtained.

This is generally the situation for processing gibbsitic bauxites but not for boehmitic bauxites where higher digestion temperatures are used. Also for gibbsitic bauxites there are some bauxites, especially those with a low iron oxide content, that do result in high iron concentrations in liquor and consequently require some form of iron control. The reason that low iron bauxites result in high iron in liquor is generally given that iron oxides are very slightly soluble and they have a higher solubility at elevated temperatures. Also goethite, and especially aluminous goethite, can transform through a dissolution/precipitation reaction to the more stable haematite with consequent increase in iron solubility above the solubility of haematite (the equilibrium phase) [2]. To reduce the iron level in liquor to the equilibrium level during the digestion/cooling step requires sufficient seed (i.e. iron oxide surfaces). Low iron bauxites do not have sufficient seed to enable the iron in liquor to be reduced to the desired low level. One common method to overcome the issue has been to blend the low iron bauxite with a higher iron (and normally lower alumina grade) bauxite [3]. Refineries often have developed an empirical correlation relating the iron content in bauxite to that resulting in the liquor such as in Figure 1; the iron in liquor can be related directly to product iron levels. By blending the bauxites to give the required iron level in bauxite the

required iron level in product is achieved. The Suralco refinery in Suriname (a joint Alcoa World Alumina — BHP Billiton operation) blends a low-iron deep-seated bauxite with a high-iron bauxite to maintain the required product quality.

For many refineries processing a single bauxite, or refineries blending high- and low-iron bauxites, the iron level in liquor can suddenly increase or drop. Often there are no obvious changes in processing conditions and the only cause appears to have been a change in the bauxite feed even though the iron oxide content of the bauxite has remained steady. This indicates that total iron oxide content of the bauxite is, by itself, not the complete story.

An example is given in Figure 2 for a range of bauxites with varying iron levels all digested under similar conditions (145°C and a free caustic level of 150g/l expresses as sodium carbonate). Although there is a general trend of higher iron values with lower iron content, there is a large degree of scatter in the data especially for low iron content bauxites.

There is also still debate as to whether the iron in liquor is present as colloidal iron or as a soluble species. If it is present in the colloidal form it is of such a size that current filtration processes (and most laboratory ones) cannot remove it. Consequently, from a practical standpoint such iron will present to product.

To try to better understand why some bauxites give high soluble iron values in liquor and to explain and predict the observed variations, work was undertaken on a range of bauxites under varying digest conditions. These included bauxites containing various iron minerals to determine if some were more soluble than others and what were the major factors controlling the level of iron in liquor.

2. Solubility of Iron Oxides in Bayer Liquors

The effect of temperature on the solubility of iron oxide is shown in Figure 3 and indicates the expected increase in soluble iron with temperature. The iron is believed to exist as a $\text{Fe}(\text{OH})_3^-$ ion but there is limited thermodynamic and speciation data at the high ionic strengths of the Bayer process to verify that and to allow thermodynamic calculations of its solubility with respect to temperature and concentration.

The effect of free caustic concentration on the iron solubility of haematite and goethite are shown in Figure 4

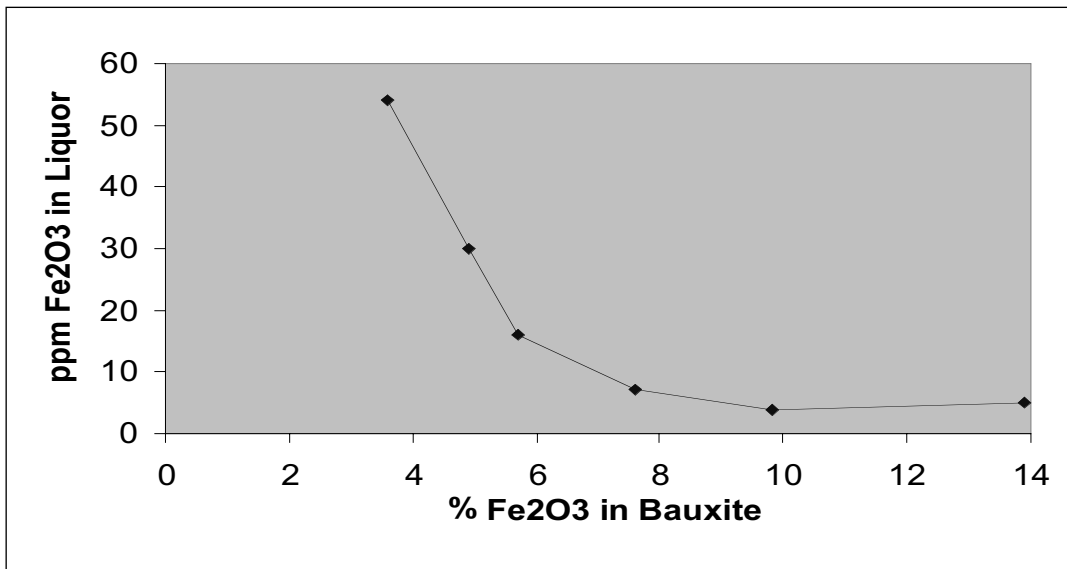


Figure 1 — Soluble iron dependency upon total iron oxide in bauxite.

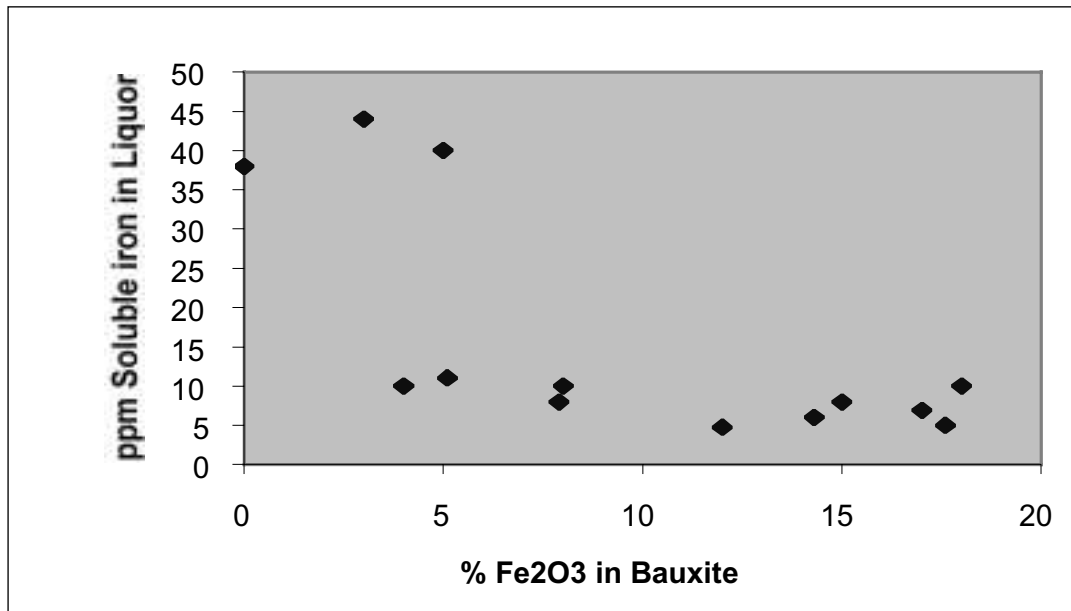


Figure 2 — Soluble iron for digestion of different bauxites.

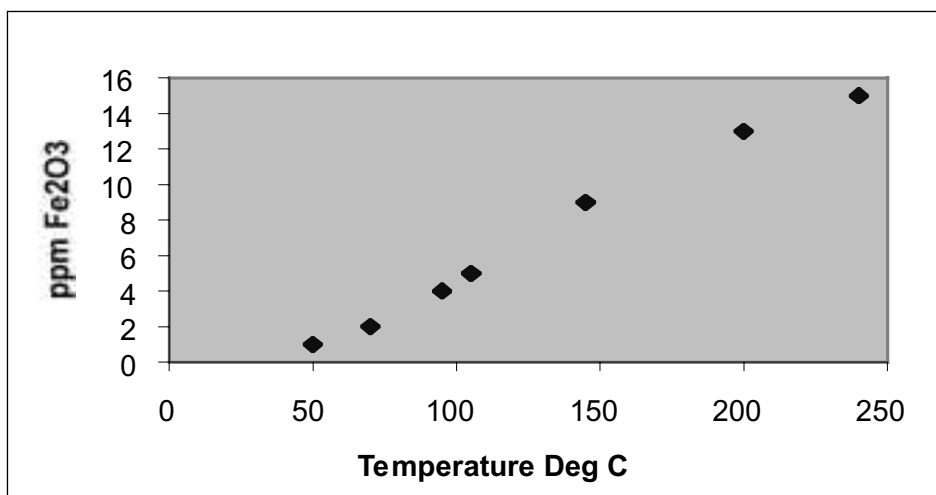


Figure 3 — Effect of temperature on iron solubility in Bayer liquor.

for digests at 145°C. Liquor samples were taken at temperature and immediately “quenched” to ensure no precipitation of iron from the liquor on cooling. For both mineral phases the iron level in liquor is less than 10ppm for liquors containing below 20%NaOH. At higher concentrations the iron level rises to high levels and is the reason why steel becomes a less favoured construction material in concentrated liquors such as evaporators where both the high temperatures and concentrations can result in significant erosion of steel. It is noteworthy that there is little difference between the iron in liquor value for goethite and haematite in these liquors.

Typical values of free caustic for green and spent liquors are 6% and 12% respectively. At those levels of free caustic the iron in liquor would not expect to cause an iron quality issue. The iron in liquor values for haematite and goethite are significantly lower than for most of the bauxites reported in Figure 2 that had been digested in spent liquor to give a typical green liquor concentration.

The effect of free caustic concentration on the iron solubility for some bauxites is shown in Figure 5. The iron

in liquor values are significantly higher than for haematite and goethite. For the low iron bauxite sample WW, the only identified iron mineral was haematite yet clearly the level of iron in liquor is far greater than that for pure haematite and is so high that it would not be able to produce a pregnant liquor meeting product specifications. Sample GG is a mixture of that bauxite and a high iron bauxite; the required iron in liquor value has been achieved although going to higher free caustic liquors would result in unacceptable iron values. The sample HH is a typical Daring Range, WA, bauxite that is processed without blending and has a high iron oxide content (typically 12–17% as Fe₂O₃). The iron oxides are about 60% aluminous goethite and 40% haematite. At high caustic concentrations that bauxite also results in very high iron in liquor values, significantly higher than the pure iron oxides.

2.1 Effect of total caustic and free caustic

To establish whether free caustic (FC) or total caustic (TC, free sodium hydroxide and hydroxide present as

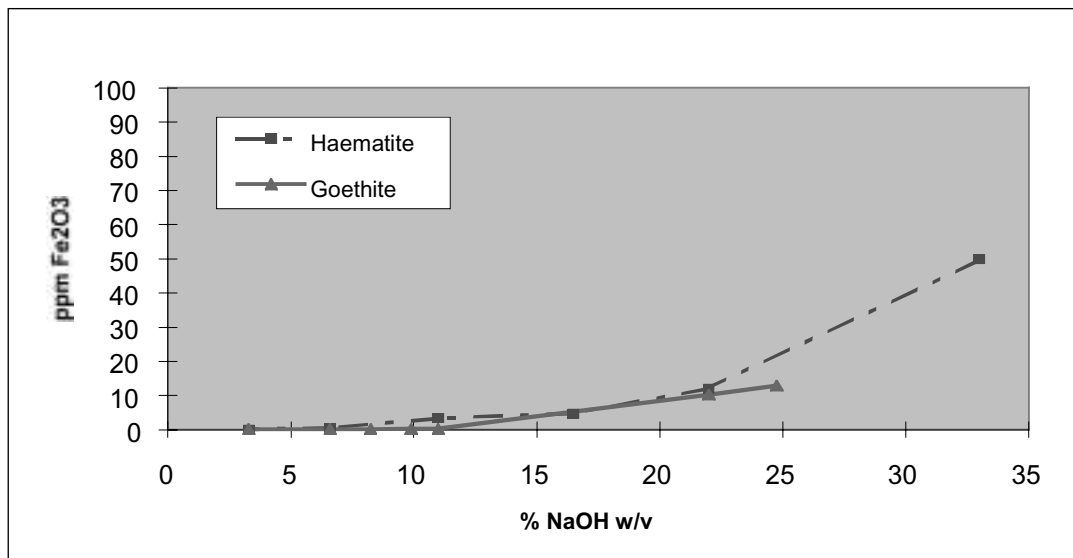


Figure 4 — Effect of free caustic on iron solubility.

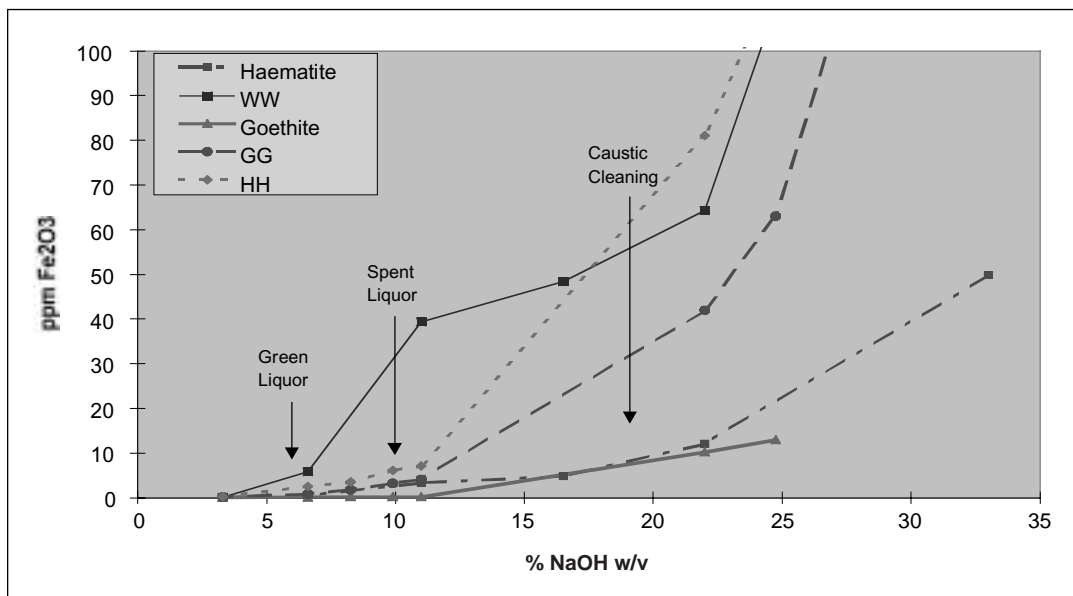


Figure 5 — Iron in liquor for iron oxides and bauxites digested in caustic.

aluminate) was the most important parameter, a sample of mud was digested in spent liquor (high FC) and green liquor (low FC) with the same TC. The data are shown in Figure 6 with samples being taken during heating and cooling of the autoclave. For the digest in green liquor there was only a slight increase of iron in liquor on digestion and the liquor returning close to its original value during the cooling cycle. For the digest in spent liquor the iron value increased dramatically from 3ppm up to 12ppm. On cooling, the iron level drops as the iron precipitates but is still significantly higher than that of green liquor at the end of the digest. This indicates that free caustic is the more significant of the variables. It also demonstrates, as expected, that kinetics clearly has an important role in determining the final iron level in solution after a digest.

Refineries processing boehmitic or gibbsitic/boehmitic bauxites result in much higher iron levels in liquor than for processing most gibbsitic bauxites. Digest conditions for such boehmitic bauxites involve temperatures often in the range of 240°C to 260°C. The free caustic concentration is a lot higher than in processing gibbsitic bauxites as a lower Al₂O₃/TC ratio is targeted in order to assist dissolution of the boehmite and achieve better extraction. The combination of the higher temperature and higher free caustic results in iron levels of the order of 10ppm after digestion. Consequently refineries processing boehmitic bauxites are particularly susceptible to producing high iron in product and may require a specific iron removal step to achieve the desired product quality. One method has been the use of sand filters to clarify the liquor as they have the potential to reduce soluble iron by enhancing the iron precipitation as the liquor percolates through a bed of iron oxide particles [3]. There have been many attempts to enhance the iron removal via treatment of the residue sand used in such filtration, but with only limited success and invariably with higher processing cost [4].

To process diasporic bauxites via the Bayer process even more aggressive conditions of temperature and free caustic are used. A specific iron removal step is required with such processing to achieve the desired product quality.

2.2 Solubility of iron from bauxites

To better understand the differences in iron solubility for different bauxites, various bauxites were reacted in typical

Bayer spent liquor and the iron in liquors monitored throughout the process. Some data are given in Figure 7. What can readily be seen is that “soluble” iron dissolves rapidly and high iron levels can be obtained with the onset of gibbsite dissolution. Indeed the iron peak appears to be obtained around 100°C and then the concentration falls as the temperature is increased. By the time digestion temperature is reached the iron in liquor has dropped to a lower and relatively constant value.

Also plotted are the data for goethite and haematite. Those minerals have very low iron solubility even at the digest temperature. Clearly other iron minerals are the major contributor to the high iron solubility.

To further assess such differences the bauxites were completely digested in spent liquor at 95°C and the iron level measured. The initial spent liquor contained less than 1ppm iron. The data are given in Figure 8 for a variety of bauxites. Again high levels of iron in liquor were achieved at this low temperature and on holding the iron content only slowly reduced.

3. Origin of the soluble iron

3.1 Iron sulfide minerals

Iron can exist as pyrite or other sulphides in bauxites but in all but one of these bauxites there was no detectable sulfur as sulfide and no indication of iron sulfide minerals. Samples were subjected to a dilute acid wash and also an acid ammonium oxalate extraction as used in soil classification. Very little iron was recovered and on subsequent treatment the samples again gave high iron values indicating the iron was not simply present as surface adsorbed iron (possibly as an organic complex) or as poorly disordered and x-ray amorphous ferrihydrite or siderite.

The iron sulfide minerals are relatively unreactive in the Bayer process as the liquor is predominantly under reducing conditions (especially with significant levels of organics present). However, such iron sulfide minerals can result in high soluble iron. First if they are left to oxidise prior to processing (they are very prone to bacterial action), then the iron may be as a soluble form. Secondly such pyrite does not act as a seed for iron precipitation. Hence bauxites having 3% Fe₂O₃ as measured by XRF that is present as pyrite have effectively no iron present to act as seed for iron precipitation. Consequently for relationships

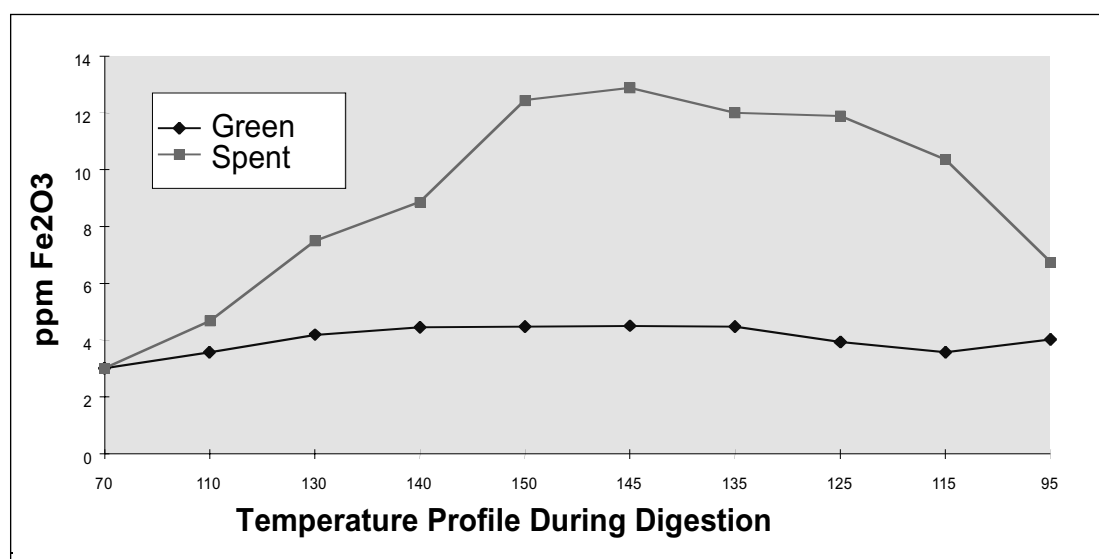


Figure 6 — Digestion of a red mud residue in green and spent liquor.

as shown in Figure 1 it is necessary to determine whether the iron is present as oxide or sulfide.

3.2 Iron present in gibbsite

The samples that gave very high iron levels in liquor and were low in iron in bauxite were washed with hot spent liquor at high solids such that little gibbsite could dissolve. Little iron was obtained in solution. On reacting the caustic washed bauxite in further spent liquor at low solids such that all the gibbsite could dissolve, a high iron in liquor value was obtained. This indicated that the source of the iron for these low iron bauxites was predominantly from the gibbsite itself.

In the Bayer process the iron in the liquor precipitates in the initial stages of the precipitation process within the

gibbsite and concentrates in layers. Hence the iron is not uniformly distributed in the gibbsite particles but is concentrated on the edges of the bands such as can be seen in Figure 9. Furthermore, various iron oxides and aluminium oxides are isomorphous and there is considerable aluminium substitution in goethite and similarly there can be considerable iron substitution in aluminium oxide/hydroxides. Hence it is postulated that with low iron bauxites, where there is little iron oxide seed present, a large amount of iron is precipitated within the gibbsite during the bauxitisation process. Such iron would be readily solubilised when the gibbsite dissolves. The iron content of the gibbsite needs only to be 0.10% maximum to explain all the soluble iron; gibbsite containing such high iron values can readily be formed by spiking liquors with iron prior to precipitation.

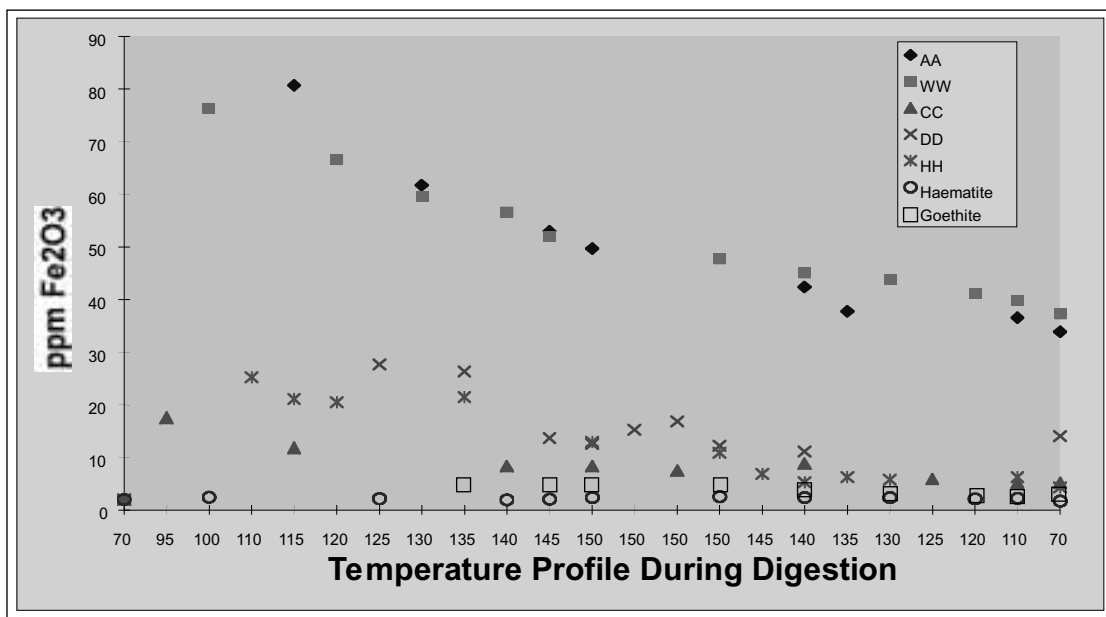


Figure 7 — Digestion Profiles of Various Oxides and Bauxites.

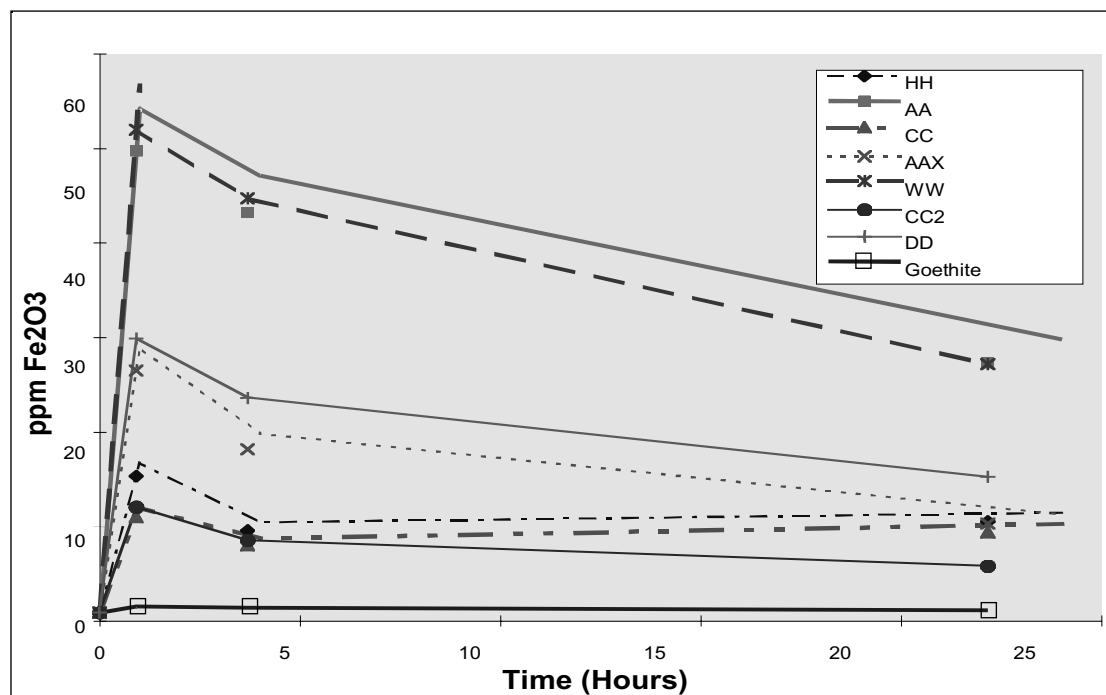


Figure 8 — Various Bauxite Samples Dissolved at 95°C.

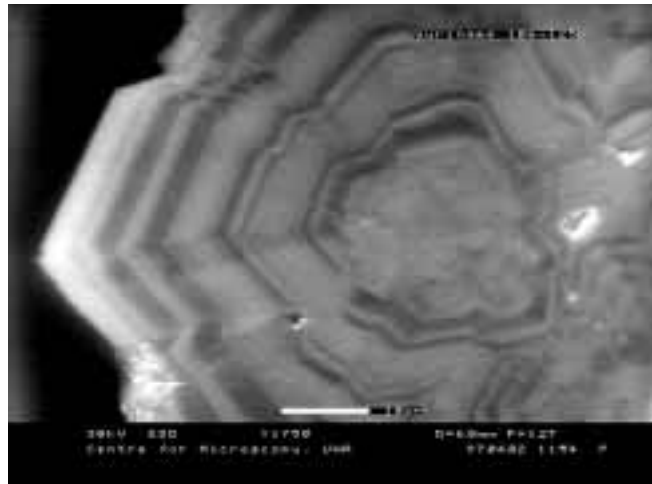


Figure 9 — Charge contrast image of hydrate showing bands.

4. Prediction of iron in liquor

From the above, it is clear that there is a need to know not only the total iron in the bauxite that assists in precipitating the iron in liquor but, as importantly, also the level of soluble iron in the bauxite. The soluble iron is not related to the iron in bauxite and is not readily measurable by such techniques as x-ray diffraction. A method has been devised that consists of dissolving the bauxite in caustic at 95C such that all the gibbsite dissolves. This releases the soluble iron in the gibbsite and gives a soluble iron number for the bauxite. That value can be a useful indicator of whether the bauxite will result in high iron levels in liquor. In Table 1 values for total iron and soluble iron are given for a variety of bauxites. As expected, there is no specific relationship between soluble and total iron. Those bauxites having a high soluble iron will require a higher level of iron oxide seed in the bauxite to help reduce that value.

The addition of a high iron oxide bauxite to reduce the iron in liquor has a two fold benefit. The first, and well recognised, effect is to increase the level of seed for iron precipitation. However the major benefit is that high iron oxide bauxites invariably have a low soluble iron content as there was sufficient iron oxide present that the iron precipitated as iron oxide rather than within the gibbsite during bauxitisation. Blending the high iron oxide bauxite with the low iron oxide bauxite thus reduces the soluble iron content. The higher iron oxide content of the mud further assists by aiding iron oxide precipitation to further reduce the iron value.

This soluble iron test is now utilised if low iron bauxites that might contain high soluble iron levels are to be

processed and is a useful test for evaluating bauxites generally with respect to their potential iron behaviour.

Table 1 — Soluble Iron Test Results

Bauxite	% Fe ₂ O ₃ in Bauxite	ppm Fe ₂ O ₃ in Caustic
AA	3.5	8
WW1	0	37
DD	3	14
CC	14	4
HH	16	7
HHH	15	8
HHJ	17	6

5. Conclusions

In Bayer processing the iron level ex-digestion is related to both the processing conditions and to the nature of the iron in the bauxite.

High free caustic and high digestion temperatures both result in higher level of iron in liquor and consequently processing of boehmitic bauxites will tend to produce high iron in product.

Bauxites can contain high levels of caustic soluble iron, especially those of low iron oxide content. The iron appears to be contained in the gibbsite and released on digestion of that gibbsite.

The high iron gibbsite is believed to have formed because of low levels of iron present in the weathering process such that there was insufficient iron oxide seed for it to be precipitated as a separate phase. Consequently it was precipitated within the gibbsite.

References

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