A Review of Zinc in Bauxites, the Bayer Process, Alumina and Aluminium

György (George) Bánvölgyi
Senior Process Consultant, Alumina
Budapest, Hungary
Corresponding Author: gbanvolgyi@yahoo.com; gbanvolgyi@gmail.com

Abstract

Karst bauxites contain significantly higher amounts of Zn compounds than lateritic bauxites, in several cases by an order of magnitude. Until very recently little information was available about the minerals in which the minor elements, such as Zn are found. Dosing Na₂S, the traditional way of Zn removal from the Bayer circuit has various drawbacks. It was proven that other metals, such as Cu and Pb react simultaneously with hydroxozincate. This is why no clear stoichiometry between sulphide and Zn in liquor can be established. The ZnO which enters Bayer precipitation circuit ends up in the product almost quantitatively and then in aluminium metal. The Zn impurity reduces the current efficiency in the electrolysis and is detrimental to the quality of the metal. The paper reviews the historical and recent fundamental research on Zn in bauxites, its behaviour in Bayer process and also the basics of Zn removal processes. A tentative ZnO balance is presented for a refinery, where most of the data are in good agreement to assist in understanding what happens with Zn in the course of processing a karst bauxite with a high temperature digestion. Application of effective Zn removal solutions becomes more and more important as the customers require alumina product with less impurities than before.

Keywords: Zn in bauxites; removal of Zn; Zn in alumina; Zn in aluminium

1. Introduction

A moderate amount of information is available regarding which minerals the various accessory and trace elements in bauxites can be found, to what extent they dissolve in the Bayer liquor, how these elements can be removed, if necessary. As Sajó [1] points out, conventional X-ray diffractometry (XRD) has a limited level of detection (typically 0.5-1 %, in some cases 0.05-0.1 phase %), and the amount of the minor minerals in bauxite are below or well below these limits.

Over the years it became clear that the conventional methods of Zn removal have various drawbacks. New methods have been developed, which are less problematic for the operators and/or result in less investment and operating costs.

The objective of this paper is to provide an overview on the occurrence of Zn minerals in bauxites, the behaviour of the Zn compounds in the Bayer process, the basics of known and practised Zn removal methods and the detrimental of Zn to the aluminium metal.

2. Occurrence of Zn in Bauxites

2.1. Zn in Karst Bauxites

Bárdossy [2] found sphalerite (ZnS) in bauxite samples from Gánt, Hungary having a size of 20-30 µm. He referred to Beneslavsky, who had discovered the same mineral in small amounts together with chalcopyrite (CuFeS₂), in bauxites from the Northern Ural, and also to Gorbachev, who had reported sphalerite within tubular formations of pyrite and marcasite (both FeS₂) in a...

In karst bauxites from Jamaica Zn was found in mineral woodruffite (2(Zn,Mn),5MnO$_2$.4H$_2$O) by Strahl [4]. Ostap reported [5] that the total ZnO content in bauxites of Jamaica vary from 0.02 to 0.1 %. The bauxite from Jamaica, which was extensively tested in the course of development of the US Patent 2,885,261 [6] had a ZnO content of 0.025-0.037 %.

Scavnicar reported [7] among other constituents, the Zn content of 47 karst bauxite samples from Herzegovina. The ZnO content was found to be 0.012-0.025 % in 42 samples while it was 0.037 % in four bauxite samples, and 0.05 % in one.

Logomerac reported [8] that the bauxite at Titograd (now Podgorica, Montenegro) contained 0.035 % ZnO. At that time the alumina refinery in Titograd was not built yet.

Perczel and Miklós found [9] ZnO contents of 0.0096 %, 0.0077 % and 0.0146 % in bauxites processed in the Hungarian alumina plants of Ajka, Magyaroévár and Almásfüzitő, respectively. It is understood that the Ajka and Magyaroévár alumina plants traditionally obtained bauxite from the Halimba and Nyirád mines, while Almásfüzitő from the Iszka mine. The goethite content in the bauxites from the Halimba and Nyirád mines was negligible, while bauxite from the Iszka mine contained fairly high amounts of (alumino-)goethite. Papp et al. reported [10] that the mined bauxites in Hungary had a typical ZnO content of 0.0124 %.

Lindsay summarizes [11] the Zn problem as follow: ZnO appears above trace levels in only a few specific sources of bauxite. Bauxites from Jamaica, the Balkan Peninsula and parts of China have elevated levels of zinc that also appear in smelter grade alumina, SGA.

See and Feret studied [12] two bauxite samples from Jamaica which contained 0.02 % and 0.03 % ZnO. In these bauxites ZnO was found in hematite, goethite, ilmenite in moderate amounts, significantly more in hydrated Ti-Fe phases (leucoxene) using various state-of-the-art investigation methods.

Feret and See claimed [13] that Zn can be found in gahnite (ZnAl$_2$O$_4$) and sphalerite in Caribbean bauxites. They reported discovery of a new mineral in bauxites from Jamaica, which was named zincophorite having a chemical formula of Al(Zn$_{x}$Mn$_{1-x}$)O$_2$(OH)$_2$. The x might vary from 0.02 to 0.24. In this paper Feret and See challenged that Zn could really replace Fe in the goethite lattice. The synchrotron-generated radiation is advocated as producing a significantly enhanced quality of diffraction which allows more detailed study.

Suss et al. state [14] that in Russian Northern European and Ural karst bauxites Zn is associated with chamosite. In the case of Jamaican bauxites removal of iron-manganese concretions can be a means of reducing ZnO-input. It is reported that Niksic bauxite (Montenegro) has an average ZnO content of 0.0436 % ZnO, while bauxites from Jamaica contain 0.05 % ZnO. Two Russian bauxites from Northern Ural (SUBR) 0.024 % ZnO, from Timan (Komi Republic) 0.075 % ZnO were also reported. The maxima are obviously higher than the avarages, where indicated. In the case of SUBR bauxite the maximum ZnO content was found to be 0.75 %.

Guoyao et al. reported [15] Zn in bauxite processed at Pingguo Alumina Plant in minerals such as zincblende (β-ZnS) and smithsonite (ZnCO$_3$).

Komlóssy deems that sphalerite is the most important source of Zn in bauxites [16].
2.2. **Zn in Lateritic Bauxites**

In a characteristic lateritic (gibbsitic) bauxite sample from Fria, Guinea, the zinc content was found to be to 0.0034 % ZnO [17].

See and Feret studied [12] lateritic bauxites which contained 0.00 or 0.01 % ZnO.

In the Eastern Ghat bauxites (India) 71 ppm (0.0071 %) ZnO was claimed by Goyal et al. [18].

The lateritic bauxites of CBG (Guinea) contain 0.0015 % ZnO and the Trombetas bauxite (Brazil) 0.0083 % ZnO. These values are claimed by Suss et. al. (2015) to be averages [14].

Lindsay [11] mentioned Minas Gérais bauxite in Brazil as a lateritic bauxite marked with elevated Zn content.

It should be noted that ZnO content in lateritic bauxites is typically significantly less, possibly by an order of magnitude than for karst bauxites.

3. **Behaviour of Zn-Compounds in the Bayer Process**

As per Ostap [5] the reaction of the ZnO content of bauxites in Bayer liquor can be described with the following equation:

\[ \text{ZnO} + 2 \text{NaOH} \rightarrow \text{Na}_2\text{ZnO}_2 + \text{H}_2\text{O} \]  \hspace{1cm} (1)

At the low temperature digestion conditions (~ 143 °C) the extraction of ZnO is as low as 10-20 %. Ostap also claimed that when goethite was converted to hematite in high temperature digestion in the presence of the large lime charges needed to convert (alumino-)goethite to hematite, essentially complete extraction of Zn could be attained. Under these conditions greater extraction of V and Cr was observed suggesting that not only aluminium can replace iron in the goethite lattice (FeO(OH)), but Zn, V and Cr as well.

Verghese disclosed [19] that the zinc minerals in bauxite partly dissolve in the course of digestion as sodium zincate and the amount which gets to the precipitation area almost quantitatively ends in the product hydrate. In the plants where bauxites with high zinc content are processed, excess zinc is precipitated as insoluble zinc sulphide by the addition of sodium sulphide prior to the security filtration of pregnant liquor. The detrimental effect of this operation is that the unreacted sulphide gradually oxidises to sulphate which accumulates in the process liquor circuit and is harmful to the precipitation unit operation. One more issue is the corrosion problems caused by the high level of Na₂S.

Bujdosó and Tóth reported [20] that the ZnO content of the pregnant liquor completely precipitates with the hydrate. Teas and Kotte claim [21] that some 90 % of the ZnO in the liquor to precipitation gets into the product hydrate, and eventually into the product.

P.J. The claims [22] that the Zn in the Bayer liquor is as ZnO\(_2^2\) or Zn(OH)\(_4^2\) ions. Based on experiences with dissolved silica and alumina in the process liquor, the author of the present paper deems the Zn(OH)\(_4^2\) form is more probable. According to The, the zincate or zinc hydroxide ions are in a fine colloidal form due to the alumina and carbonate ions in plant liquor. There are other ions in the process liquor which also react with sulphide ions, in the case of sodium sulphide addition. Therefore the reaction between zincate or Zn hydroxide and sulphide ions is by no means stoichiometric, and an excess sulphide dosage is required. More than half of the sodium sulphide remains in the process liquor and eventually oxidises to sodium sulphate. The sodium sulphate concentration can reach as much as 50 gpl, which reduces the precipitation...
yield and leads to slightly finer aluminium hydroxide product. The high sodium sulphate content in the liquor can be responsible for the fragility of the product hydrate and increased soda impurity in product. These data obviously relate to the so-called American Bayer liquors, where traditionally higher level of contaminants were tolerated than in the European alumina refineries which operate with higher precipitation yields. Cu is certainly one of the metallic ions, which competes for the sulphide ions, others are not specified.

Perczel and Miklós [9] in their dissolution tests with Hungarian bauxites found about 50 % dissolution of ZnO at 180-200 °C.

It is deemed that the reactions of zinc hydroxide with sodium sulphide and also the dissolution of sphalerite in the course of digestion can be well described by the following equation:

\[
\text{Na}_2\text{Zn(OH)}_4 + \text{Na}_2\text{S} \rightleftharpoons \text{ZnS} + 4\text{NaOH} \quad (2)
\]

US Pat. 2,885,261 [6] educates that about half of the zinc dissolves from bauxite in the course of (high temperature) digestion. Some dissolved zinc precipitates during clarification and eventually approximately 30 % of the zinc charged with the bauxite remains in the pregnant liquor. Practically all of the zincate that gets into the precipitation area precipitates with the alumina hydrate. Two weeks after the completion of the tests some 60 % of the sulphur charged as Na\textsubscript{2}S was still in the circuit in an oxidized form.

US Pat. 3,445,186 and 3,469,935 disclose [23] that in the case where sodium sulfide is added to the blow-off (digestion effluent) slurry, colloidal ZnS forms, which can be absorbed by the red mud and travels throughout its washing. When sodium sulfide is added, beside Zn, Cu and Pb also form non-soluble metallic sulphides and are thereby removed from the liquor circuit. The ZnS colloid precipitate can partly get into the alumina hydrate, and can sublime in the course of calcination, which is carried out at 1200 °C, since the subliming temperature of ZnS is 1185 °C. The calcination temperature of the contemporary sandy alumina is only about 1050 °C, therefore the calcination can not help in the removal of ZnS any more. It is also revealed that if “salting out product”, which contains sulfate (e.g. 10.2 % SO\textsubscript{3}) is carbothermically reduced, its Na\textsubscript{2}S content is more effective from the point of view of the Zn removal than the commercial sodium sulphide.

Feret and See investigated [13] the dissolution of ZnO content of bauxites at 135 °C and 240 °C in laboratory bomb tests. At 135 °C a very small fraction of ZnO got dissolved with large variation. At 240 °C a moderate amount of ZnO dissolved and a correlation between the caustic soluble ZnO and MnO content was observed.

Suss et al. confirm [14] that Zn in the Bayer process is in the form of hydroxozincate Na\textsubscript{2}Zn(OH)\textsubscript{4}, at least in strong liquor.

4. **Target ZnO Content in the Ordinary Smelter Grade Alumina**

In the paper of The [22], ZnO in alumina of 0.023 % is specified as satisfactory level. US Pat. 2,885,261 claims [6] that if zinc in the Al metal amounts to 0.01 % it then becomes a matter of concern. In amounts above 0.02 % Zn it becomes a serious problem used for certain purposes. In the patent 0.017 % ZnO content in alumina is noted as acceptable limit, so that the metal had a Zn content of not more than 0.03 %, which was the limit of the metal sold to the government stockpile.

Lillebuen et al. compared [24] seventeen aluminas of Hydro Aluminium from different origins. The ZnO content of less than 10 ppm (0.001 %) was measured in the products of twelve
refineries which undoubtedly processed gibbsitic type lateritic bauxites with low temperature digestion. Five aluminas contained 80 or 90 ppm (0.008-0.009 %) ZnO, indicated the refineries operated high temperature digestion.

H. Oye in his fundamental paper [25] on aluminium smelting recommends a ZnO content of less than 125 ppm, i.e. < 0.0125 % in alumina. This amount of ZnO results in 0.0193 % in aluminium metal, which meets the widely accepted specification of Al metal of < 0.02 % Zn. A factor of 1.92 t alumina/t Al metal is used for such conversion. Suss et al. recommend [14] a specification of ZnO in SGA < 0.01 %.

It can be observed that the specification of alumina are different in the various geographical locations, and also, there is a trend to apply increasingly strict requirements.

5. Demonstration of the ZnO Balance

A tentative Zn balance for an alumina refinery using the high temperature digestion variant of the Bayer process in the Balkans in ZnO, g/t alumina is as follow:

<table>
<thead>
<tr>
<th>Step</th>
<th>Calculation</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>Input with bauxite</td>
<td>2.083 t/t&lt;sub&gt;a&lt;/sub&gt; * 360 g/t = 749.5 g/t&lt;sub&gt;a&lt;/sub&gt;</td>
<td>100% +/- 10 %</td>
</tr>
<tr>
<td>(Estimated 1030 kg AI&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;/t&lt;sub&gt;a&lt;/sub&gt;, dissolved alumina, 0.95*(580.5-60.1) kg/t bauxite)</td>
<td></td>
<td></td>
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<tr>
<td>In red mud from digestion</td>
<td>0.93 t/t&lt;sub&gt;a&lt;/sub&gt; * 411.6 g/t = 382.8 g/t&lt;sub&gt;a&lt;/sub&gt;</td>
<td>51% +/- 5.1 %</td>
</tr>
<tr>
<td>In washed red mud</td>
<td>1.117 t/t&lt;sub&gt;a&lt;/sub&gt; * 514.8 g/t = 575.0 g/t&lt;sub&gt;a&lt;/sub&gt;</td>
<td>77% +/- 7.7 %</td>
</tr>
<tr>
<td>In liquor to precipitation</td>
<td>13.90 m&lt;sup&gt;3&lt;/sup&gt;/t&lt;sub&gt;a&lt;/sub&gt; * 12.25 g/m&lt;sup&gt;3&lt;/sup&gt; = 170.3 g/t&lt;sub&gt;a&lt;/sub&gt;</td>
<td>23% +/- 4.6 %</td>
</tr>
<tr>
<td>In dry alumina hydrate</td>
<td>1.53 t/t&lt;sub&gt;a&lt;/sub&gt; * 159.5 g/t = 244.0 g/t&lt;sub&gt;a&lt;/sub&gt;</td>
<td>33% +/- 3.3 %</td>
</tr>
<tr>
<td>In product alumina</td>
<td>1.0 t/t&lt;sub&gt;a&lt;/sub&gt; * 152.5 g/t = 152.5 g/t&lt;sub&gt;a&lt;/sub&gt;</td>
<td>20% +/- 2.0 %</td>
</tr>
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The ZnO in the alumina hydrate is the single number inconsistent with the rest. This number can not be reconciled in the range of accuracy indicated which is 10% relative for solids and 20% relative for liquid as estimated by Papp [10]. The other values are in line with each other and experience in other refineries. In the liquid phase of clarification 749.5 -- 382.8 = 366.7 g/t<sub>a</sub> ZnO could have been found. With this amount of ZnO, 0.35 kg/t<sub>a</sub> of 100% Na<sub>2</sub>S would have been the the stoichiometric requirement. It is estimated that some 7.8 kg of 100% Na<sub>2</sub>S (purity) was actually used which means, that 22 times more sodium sulphide might have been applied than the sodium sulphide and zinc hydroxide stoichiometry.

6. Processes Developed to Reduce the ZnO in Pregnant Liquor

US Pat. 2,885,261 suggests [6] that the red mud settler overflow is a convenient point for sodium sulphide addition. Some 60% of the sodium sulphide added to the process increased the liquor sodium sulphate concentration due to its oxidation to thiosulphate, sulphite, polysulphide and finally sulphate. The sulphide addition is therefore an obvious source of the sulphate in process liquor. The desilication product (DSP), however, serves as a sink for sulphate anions. Half of the total pregnant liquor stream is suggested for the removal of ZnO content. In this case the removal is more effective than if the whole liquor stream were treated, and there is a lower sulphate accumulation. The recommended sodium sulphide concentration should be higher than 0.2 g/l, preferably at least 0.4 g/l. As a consequence of parallel reactions, no clear stoichiometry for ZnO removal has been established. The temperature range of the pregnant liquor stream is between 66 and 93 °C. Better Zn removal efficiencies were obtained at lower temperatures. This observation contradicts the requirements for an effective security filtration.
The US Pat. 3,445,186 and 3,469,935 propose [23] that Na₂S can be reacted with dissolved sodium zincate in the blow-off slurry. The method was summarized earlier in this paper and it was implemented in several alumina plants with some variations.

In the case where sand particles are coated with sodium sulphide prior to their use for pregnant liquor security filtration and at the same time for reducing the liquor ZnO (and CuO) content. Up to 75% of zinc and copper can be removed from the process liquor in sand bed filters according to The [22] and US Patent 4,414,115 [26]. However, sand bed filters have numerous drawbacks. Discussion of these difficulties is beyond the scope of the present paper.

The US Patent 4,282,191 suggests [27] using freshly synthetized ZnS seed along with Na₂S to form ZnS out of sodium zincate (or Zn-hydroxide) formed during the digestion of bauxite. The ZnS seed is synthetized from ZnO (from outside source) and Na₂S. The Na₂S is added to the liquor in excess when ZnS is synthetised, so that after formation of the ZnS seed, in combination with the residual Na₂S already present in the settler overflow, an Na₂S concentration of at least 0.15 g/l, preferably between about 0.15 and about 0.18 g/l be maintained. The resulting ZnS is then removed by filtration of the pregnant liquor. The ZnO content of the pregnant liquor could thereby be reduced from 20-30 mg/l to 5-15 mg/l. This method was used in the ALPART alumina refinery (Jamaica). It is estimated that the ZnO content in the calcined alumina was about 0.008 %. It is also estimated that the ZnO consumption was about 0.08 kg, and about 1 kg of sodium sulfide was used for one ton of alumina product. The bauxite that was processed in the Alpart contained 0.028-0.030 % ZnO.

The US Patent 6,352,675 reveals [28] that dithiocarbamate and/or dithiocarbonate compounds have been found effective to remove heavy metals, such as zinc from Bayer liquor by the formation of complexes.

As per Suss et al. [14] elemental sulphur was introduced to bauxite grinding at 2-4 kg/t of alumina. A sulphide ion (S²⁻) concentration of ~ 0.25 g/l was achieved, which led to formation of ZnS (sphalerite) during digestion. This method is used in the Kamenk Uralsky alumina refinery in Russia. VAMI recently optimised the use of elemental sulphur for the removal of ZnO from the Bayer circuit in such a way that sulphur is added to the first washer liquor, the thiosulfate largely converts to sulphide and sulphite ions in the course of digestion and ZnS seed is formed.

Guoyao et al. reported [15] the improvement of the conventional Zn removal process(es) by introduction of compressed air into the diluted slurry and increase the retention time. By this way the ZnO content in the alumina was reduced from 0.015 % to 0.011 %.

7. Detrimental Effects of Zn in Aluminium Metal

Vergheese claims [19] that zinc is detrimental to some aluminium properties, such as the production of foil.

Lindsay summarizes [11] the fate of metal impurities from bauxite to the aluminium metal. A level of 100 ppm ZnO (0.01 %) in alumina contributes 154 ppm (0.0154 %) Zn in metal. Alumina is essentially the only input source for Zn in aluminium. The primary metal product of concern is extrusion billet, especially which is used for “bright” applications such as autotrim and Venetian blinds. Zinc causes the surface of metal to have a spangled appearance, not unlike that of galvanized steel, but with much smaller grains. Typically, the specification for such metal products is a maximum of 0.02 % Zn.

The expectations of some customers such as the automotive industry are for the highest level of quality. In such cases, with other factors being equal, metal producers with higher levels of Zn
in product may not enjoy the status of being a preferred supplier. Alumina producers with < 50 ppm ZnO (< 0.005 %) in product may be preferred over those with higher levels of ZnO for consumers that produce extrusion billet.

Suss et al. claim [14] that an increase of the Zn ion content in the electrolysis bath by 0.01 % reduces current efficiency by 0.13 %. Zn in aluminium metal exceeding 0.01 % impacts its mechanical properties, with the metal becoming fragile and not suitable for extrusion. Similar to gallium and titanium, zinc can also serve as an excellent finger-print tracer element.

8. Conclusions

The Zn in bauxite has been found in minerals such as sphalerite, woodruffite, gahnite, zincblende, smithsonite and the recently discovered zincophorite. It has also been detected in hematite, goethite, ilmenite and also in hydrated Ti-Fe phases (leucoxene). The karst bauxites contain significantly higher amounts of Zn compounds than the lateritic bauxites, in several cases by an order of magnitude.

In the course of the low temperature digestion of gibbsitic bauxites as little as 10—20 % of ZnO dissolves. During the high temperature digestion 50 % of ZnO or more is dissolved. The amount of zincate or zinc hydroxide that enters the precipitation area almost quantitatively gets into alumina and subsequently to metal product.

The methods which have been developed for the removal of dissolved Zn-compounds target the separation of bauxite residue and/or security filtration. Almost all are based on the addition of sulphide ions, preferably along with some sort of ZnS seed.

A ZnO balance of the process can be a useful tool to monitor the dissolution of ZnO and the removal of the same if necessary.

Today a ZnO content of about 100 ppm (0.01 %) is considered to be a reasonable specification for smelter grade alumina, though there are customers who apply more stringent critera. Application of effective Zn removal solutions becomes more and more important as the customers require alumina product with less impurities than before, first of all, in the alumina refineries, where karst bauxites are processed with high temperature digestion.

9. Acknowledgements

The Author is grateful to Dr György (George) Komlóssy and Steve Healy for their important suggestions on the manuscript and English editing.

10. References

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