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

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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 Na_2S, 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 ($CuFeS_2$), in bauxites from the Northern Ural, and also to Gorbachev, who had reported sphalerite within tubular formations of pyrite and marcasite (both FeS_2) in a

Southern Timan (Russia) bauxite. Bárdossy and Pantó detected [3] sphalerite with galena (PbS) in bauxite from Gánt.

In karst bauxites from Jamaica Zn was found in mineral woodruffite ($2(Zn,Mn).5MnO_2.4H_2O$) 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, Magyaróvár and Almásfüzitő, respectively. It is understood that the Ajka and Magyaróvár 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 %.

Linsday 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 ($ZnAl_2O_4$) 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 $Al(Zn_xMn_{1-x})O_2(OH)_2$. 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 conretions can be a means of reducting 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].

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.

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10. References

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