THE ANALYSIS OF BERYLLIUM IN BAYER SOLIDS AND LIQUIDS

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Abstract

Understanding the nature and chemistry of beryllium in the Bayer process is important to enable opportunities for the removal or control of beryllium in alumina to be implemented. This paper presents chemistry and analytical techniques that are relevant to the study of beryllium within the aluminium industry. The use of NanoSIMS to detect beryllium in hydrate is presented for the first time.

1   Beryllium in the aluminium industry

In the aluminium industry the potential for exposure to beryllium manifests itself in some smelters where it is present in the smelting pots at parts-per-million (ppm) levels. Removal of scale (crust) from affected areas can generate dusts containing beryllium. To eliminate the potential risk of overexposure to beryllium in the potroom environment, the aluminium industry would prefer to reduce the levels of beryllium in the alumina below the level for potential risk for the potroom environment.

Beryllium enters the smelting pots as an impurity present in some smelting grade aluminas (SGA). Beryllium has a great affiliation for fluoride and once it dissolves in the pots (with the alumina) only a small proportion leaves through the normal smelting exits (metal, cathodes and losses). Instead, most of the beryllium remains in the baths (Figure 1) and the concentration builds up until there is a change in the beryllium input (by introducing alumina with a lower beryllium content) or it reaches a solubility limit (not yet determined).

The source of beryllium in alumina is trace levels present in some bauxite deposits. The average concentration of beryllium in the Earth's crust is 2.8-5.0ppm (Reeves, 1986). Beryllium compounds are naturally present in soils and surface rocks at trace concentrations ranging from 0.01 to 40ppm (Bowen, 1979). The typical soil concentration in the USA (for example) is 0.6ppm. Natural beryllium concentrations >5ppm can be considered to be enriched and beryllium-bearing veins can contain >50ppm beryllium.

In common crystalline rocks, beryllium is enriched in the feldspar minerals such that 85-98% of the total crustal beryllium may be bound in the feldspar structures (Beus, 1966). A biochemical study in the Czech Republic (Navratil *et al*, 2002) found that plagioclase had the highest beryllium concentration out of the rock-forming minerals and that the Be in K-feldspar was due to impurities inside the grains. The greatest known concentrations of beryllium are found in certain pegmatite bodies and it is sometimes concentrated in hydrothermal veins. Some granitic rocks contain sufficient amounts to permit the crystallization of small amounts of beryl. During the weathering of crystalline rocks and sedimentation processes, beryllium seems to follow the course of aluminium and becomes enriched in some bauxite deposits, clays, and deep-sea sediments. Beryllium enrichment occurs in some of the karst bauxites found in Russia, China and Hungary (Grew, 2002; Bardossy, Gyorgy, 1982).
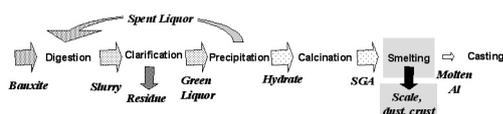

Figure 1. Transport of beryllium from bauxite to smelting pots (shading of arrows represents relative concentrations).

Our research found that some of the beryllium in bauxite dissolves during digestion. Consequently affected refineries have trace concentrations of beryllium in their liquor streams. A proportion of the beryllium in the liquor exits with the hydrate during precipitation and remains in the SGA. This can potentially present problems at the smelters when the beryllium becomes concentrated in the smelting pots.

During the smelting process SGA is added to pots containing molten electrolyte (cryolite and fluorspar). Released oxygen combines with a carbon anode to escape as carbon dioxide and the metallic aluminium is deposited on the bottom of the pot. The process is continuous with molten aluminium regularly syphoned off into mobile ladles and more ingredients are fed in automatically or manually from a mobile storage vehicle. During the process a crust forms on top of the molten liquid and this is broken up at intervals, either automatically by machinery incorporated in the superstructure or manually by a mobile crust breaker. This process can liberate beryllium-enriched dusts.

Thus to control the amount of beryllium in the smelters the problem can be addressed where it exists (at the smelters) or controlled at the source (by lowering the concentration of beryllium in alumina). Research teams at Alcoa are investigating both scenarios. In both cases an understanding of relevant beryllium chemistry is required.

2   Beryllium chemistry

There is little information in the literature specifically relating to beryllium in Bayer liquors and most of the industrial chemistry of beryllium is based on its equilibria in aqueous solution. Nonetheless some key chemical interactions in alkaline solution have been reported. This is due to both the strong interest in nuclear processing, aerospace and microelectronics applications and growing concerns about the toxicity of beryllium compounds.

There are many similarities between the chemistry of beryllium and aluminium. For example beryllium metal exposed to air forms an oxide coating which protects it from further oxidation. More interestingly, although beryllium is in the same periodic group as magnesium and calcium its solution chemistry has many similarities with aluminium, zinc and gallium. Beryllium is amphoteric and can exist as both mononuclear and polynuclear species, with the likely formation under alkaline conditions of $Be(OH)^+$, $Be(OH)_3^-$, $Be(OH)_4^{2-}$ and $Be_3(OH)_3^{3+}$ (Alderighi *et al*, 2000). Based on this information and a comparison to aluminate chemistry, the predominant species is likely to be the beryllate anion ($Be(OH)4_2^-$) in concentrated sodium hydroxide solutions such as Bayer liquor.

Crude mass balances for beryllium have been conducted at aluminium smelters but the fate and transport of beryllium in the smelter is still not well understood. It has been shown (Lewis, 1948) that in the aluminium smelters, beryllium oxide in alumina reacts with cryolite (Na_3AlF_6) to form Na_2BeF_4 according to the reaction below (Eq.1). The reaction proceeds virtually to completion at 1000ºC so that nearly all the Be in the melt is present as Na_2BeF_4. There are analogous reactions in the beryllium refining industry.

$$3BeO + 2Na_3AlF_6 \rightarrow 3Na_2BeF_4 + Al_2O_3 \qquad (1)$$
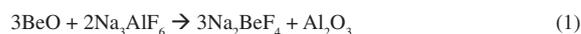
The two most important ores mined for the intentional recovery and refining of beryllium are beryl ($3BeO.Al_2O_3.6SiO_2$) and bertrandite ($Be_4Si_2O_7(OH)_2$). The two methods used for extraction of beryllium oxide from these mineral ores are the fluoride and sulphate processes. In the fluoride process (Darwin, 1960) beryl is sintered with sodium silicofluoride ($NaSiF_6$) or sodium fluoroferrate (Na_3FeF_6) to form

sodium beryllium fluoride (Na$_2$BeF$_4$). This water soluble salt is then leached with water and beryllium hydroxide precipitated from solution using sodium hydroxide.

In an ideal sulphate process (Darwin, 1960) beryllium-containing ore is digested with sulphuric acid to form beryllium sulphate in solution. Aluminium sulphate and other impurities are also extracted. Ethylenediaminetetraacetic acid (EDTA) is added to retain impurities in solution whilst sodium hydroxide is added to precipitate beryllium hydroxide.

In reality the flow diagram for recovery of beryllium is considerably more complicated. Brush Wellman use a counter current extraction process based on the sulphate method (Deubner, 2001). To separate impurities from the acidic beryllium sulphate solution, kerosene containing di(2-ethylhexyl)phosphate is used. Repeated mixing of the aqueous solution and the organic extractant in a counter current flow pattern is required to extract the beryllium into the organic phase. The aqueous phase containing most (not all) of the aluminium impurity is removed.

Beryllium is stripped back to an aqueous phase as ammonium beryllium carbonate through the use of an ammonium carbonate solution. Any remaining aluminium and other impurities (such as iron) are precipitated as hydroxides or carbonates by heating the strip solution to 70°C. The filtrate is then heated to 95°C to precipitate beryllium carbonate, which is separated and processed further to beryllium hydroxide.

Beryllium hydroxide decomposes to beryllium oxide when heated at elevated temperatures (decomposition commences at 190°C) (Patnaik, 2003). It is soluble in acids and hot concentrated caustic soda solution but is practically insoluble in water and dilute alkalies. Specifically, precipitates of beryllium hydroxide occur in the range pH 5.8 – 9. The reported pH for the start of alkaline dissolution ranges from pH 9 to 10; by comparison aluminium hydroxide dissolves in alkali at pH 9.75 (Schmidbaur, 2001). The solubility product of beryllium hydroxide is reported as log $K^0_{sp} \approx -21.6$, which would give a concentration in water of about 10^{-7} M. The thermodynamic solubility is much higher in alkaline solutions, with (for example) 0.02M in a 2M sodium hydroxide solution (Lambert & Clever, 1992).

Three forms of beryllium hydroxide are reported – a metastable tetragonal crystalline solid (alpha form), a stable orthorhombic crystalline solid (beta form) and a slimy gelatinous substance in slightly basic pH (amorphous form). It seems likely that precipitation of beryllium hydroxide from aqueous electrolyte solutions initially yields the amorphous form which is gradually transformed to the beta form under most circumstances (Lambert & Clever, 1992). This type of behaviour is determined by kinetic (mechanistic) constraints, not relative thermodynamic stability (Bear & Turnbill, 1965). The exact nature of the precipitate would therefore depend on factors such as the concentrations, method of mixing, temperature and the aging time.

Precipitation of 'sodium beryllate' solutions to produce the beta form is said to be similar to precipitation from sodium aluminate solutions (Hostache et al, 1968).

3   Determination of beryllium in Bayer solutions

For our research an Inductively Coupled Plasma – Optical Emission Spectrometer (ICP) method has been developed to analyse beryllium in Bayer process solutions. The technique was chosen because of its inherent capabilities (simple sample preparation, wide dynamic range, minimal interferences, fast analysis, etc) and because the authors have considerable experience developing successful ICP methods for Bayer liquors.

For a typical ICP method a diluted, acidified solution containing target analyte(s) and internal standard(s) is pumped into a nebuliser that turns the analyte liquid into droplets. The largest droplets fall out into a drain at the bottom of a spray chamber and the finest droplets are carried by argon gas into a radio-frequency induced argon plasma. Light is emitted by atoms and ions in the plasma at wavelengths that are characteristic of each element, with the intensity proportional to the amount. The intensity is compared to calibration curve to determine the concentration for the analyte(s) of interest.

For the analysis of beryllium in solutions such as Bayer liquor typical sample preparation involves addition of concentrated nitric acid (BDH AnalaR, 70%) to a mixture containing test liquor, internal standard solution and (deionised) water such that the final proportions are 2:1:1:6. Samples containing high concentrations of humic acids can be more difficult to prepare as they froth excessively on addition of concentrated nitric acid. Preparation in such cases involves addition of the nitric acid in a large beaker and transfer of the acidified solution to the ICP analysis vial once the sample had cooled to room temperature.

Standard laboratory safety practices (PPE, etc) are used when handling alkaline Bayer liquors and acids. Additional care is taken when handling beryllium standard solutions, especially stock solutions for ICP. Although these solutions are dilute (beryllium up to 0.1M), if they are allowed to spill and dry there is a potential risk of accidental contact with beryllium salts. Therefore such samples are handled by specially trained operators in designated areas using spill collection trays with detailed cleaning and disposal regimes.

For beryllium the available emission lines on the Perkin Elmer Optima 3000ICP are at wavelengths 234.861, 265.045, 313.042 and 313.107nm. It was determined through the technique of standard additions that the Be 234.861 emission line (with Li at 670.784nm as internal standard) gave the most accurate results. Care is required during baseline selection to avoid inaccuracies from adjacent peaks (Figure 2) for iron (234.830nm), vanadium (234.830nm) and titanium (234.841nm). Vaessen and Szteke (2000) made note of the interference from high concentrations of iron during analysis of food and drinking water samples.

When the baseline is correctly set the results from using this wavelength have a long term (between batch) measurement uncertainty of 7% (1s) and a detection limit for beryllium of 0.015mM. The Be 313.107 line is more sensitive and able to detect the presence of beryllium as low as 0.005mM however the measurement uncertainty is greater (14%,1sd).

For many Bayer solutions the presence of iron and vanadium cannot be avoided so to minimise the risk of incorrect reporting of results the beryllium is recorded using both the 234 and 313nm wavelengths. If the difference between the results is substantial (>15%) then the baseline is checked for interference. To date the authors have used the 234.861 line to accurately analyse beryllium in Bayer-like solutions containing up to 0.6mM of iron and 8mM of vanadium.
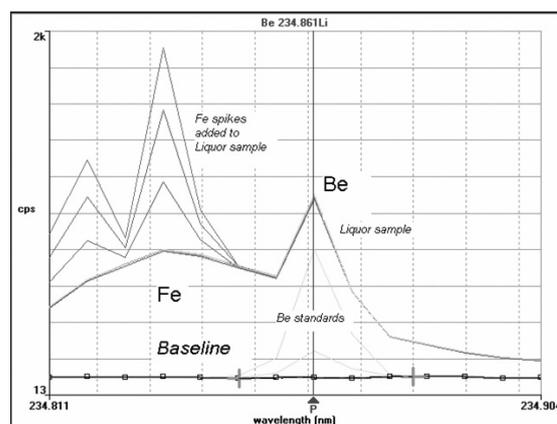

Figure 2: Raw ICP spectral data for 234.861 wave length showing interference from iron on the baseline for a liquor sample spiked with beryllium.

4   Determination of total and extractable beryllium in bauxite

Analysis of total beryllium in Bayer solids (bauxite, digest residue, hydrate or alumina) is accomplished by an acid digest followed by ICP mass spectroscopy (ICP/MS). Whilst a relatively simple acid digest using hydrochloric acid can be used to dissolve the beryllium there is an advantage in using a multi-acid digest (hydrofluoric (caution), nitric, hydrochloric and perchloric acids) in that many other trace metals are dissolved at the same time and can be simultaneously determined using ICP and ICP/MS methods.

Typically 0.3g of bauxite is digested in 50mL of acid, while the final dilution can be in the order of 1/2600. The beryllium method has a between batch measurement uncertainty (%RSD) of 6% and a reporting detection limit of 0.1ppm.

Our research has shown that for most bauxite samples only a proportion of the total beryllium present dissolves during bauxite digestion. The amount depends on the bauxite mineralogy, the liquor composition and (to a lesser extent) the digest conditions. Therefore to enable comparisons between different bauxites a standard procedure for reporting extractable beryllium has been established.

The method is intentionally similar to standards methods used within the industry for determining bauxite properties such as available alumina, reactive silica, oxalate and carbonate. In these methods and in the extractable beryllium method 100 g/L of bauxite is digested for 20 minutes at 145°C in a solution of 2M sodium hydroxide (Grocott, 1988). A sub-sample of the product filtrate is then analysed for beryllium using the ICP method described above. A correction can be made for the change in density caused for gibbsite dissolution. The advantage of using a common digest procedure is that provided a suitable digest volume is used a single digest can be used to determine and compare several or all of these bauxite properties.

Laboratory mass balances (see Eq. 2 for an example using a randomly selected bauxite sample) using the described solution and solid methods show an error of only 4%, which is well within the measurement uncertainty of the analytical techniques.

$$[Be]_{bx} + [Be]_{NaOH} \rightarrow [Be]_{res} + [Be]_{filt} \quad (2)$$
$$5.5 \times 10^{-6} + 0 \rightarrow 2.5 \times 10^{-6} + 2.8 \times 10^{-6} = 5.3 \times 10^{-6} \text{ moles}$$

5 Detection of beryllium in hydrate (NanoSIMS)

Knowledge of the speciation and behaviour of beryllium in Bayer materials is useful for the investigation of beryllium control strategies. However beryllium in bauxite and hydrate is present at trace levels and direct identification of beryllium species by x-ray diffraction (XRD) is not possible. Beryllium has a high permeability to x-rays, which makes it a very useful material for x-ray windows. Unfortunately, this property means that direct identification of beryllium using x-ray fluorescence energy dispersive spectrometry (XRF/EDS) is not possible.

Some success has been achieved using indirect methods based on secondary ion mass spectrometry (SIMS). SIMS is a highly sensitive surface analytical technique. Primary ions produced by a caesium or oxygen source are focused onto a sample surface and trigger a cascade of atomic collisions whereby atoms and atomic clusters are ejected. During this ejection process, some of them are spontaneously ionised and these "secondary ions" are a characteristic of the composition of the analysed area. Elements are identified based on their mass:charge ratios.

The NanoSIMS technique goes a few steps further and provides the capability of recording simultaneously several atomic mass images together with a high mass separation at high transmission and a high spatial resolution (Stern, 2004). The Cameca NanoSIMS 50 ion microprobe used for our research allows very fine lateral spatial resolution, theoretically in the order of 50 nm, though for the Be analysis it is closer to 500 nm because an oxygen primary ion beam must be used.

The first phase of work was to develop the methodology to detect beryllium in hydrate and to verify the outcome by suitable experiments. The outcome of that research is reported here.

A sample of hydrate known to contain some beryllium was prepared and NanoSIMS images were collected. An example image is shown in Figure 3 where detected beryllium is indicated by a white dot. The design of the NanoSIMS instrumentation limits the likelihood of erroneously displaying a signal that isn't there (noise). This is supported by the dark region in the lower right corner showing no beryllium in the mount material used for sample preparation.

Beryllium has a relatively unique mass:charge ratio so the likelihood of erroneously detecting another element (interference) is also low. Nonetheless for our research we need to be certain the image does represent the presence of beryllium.
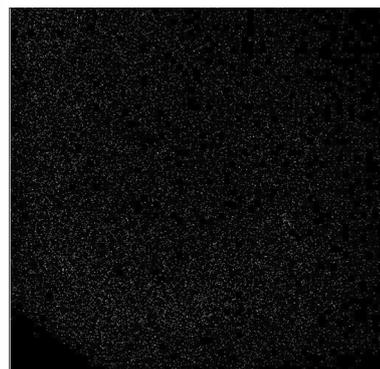

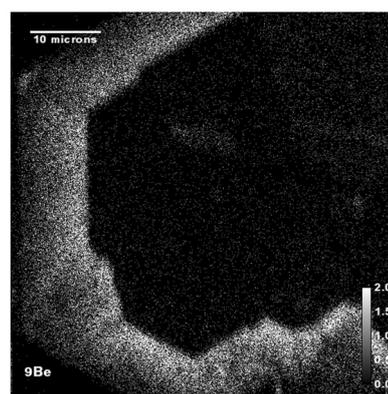Figure 3. NanoSIMS image for hydrate containing trace of Be.

Figure 4. NanoSIMS images for hydrate after precipitation from Be-rich liquor.

A confirmation test was designed to precipitate a layer of beryllium-rich hydrate around a Be-free hydrate seed. Specifically green liquor was spiked with beryllium at a concentration several orders of magnitude higher than originally present. The liquor was then subjected to a precipitation regime using 25g/L of hydrate seed and held for 90 hours at 70°C. The product hydrate was washed with copious amounts of hot deionised water and dried overnight at 60°C.

The results show a black centre (the seed) with a white halo around the edge representing the new precipitation layer (Figure 4). This is exactly what is to be expected if the instrument is truly detecting beryllium and confirms the validity of the method.

Interestingly, the wet chemical (ICP) methods reported no detectable Be (<0.005mM) in the hydrate seed, however inspection of the seed region shows what appears to be beryllium in the seed. This suggests that the NanoSIMS technique has the potential to detect the presence of beryllium at extremely low concentrations (that is, less than the detection limit of the wet chemical methods described above).

6 Mobility of beryllium in residue

As indicated earlier beryllium is usually associated in soil with aluminium sites on clay minerals and is less likely to be associated with iron oxides (Lum, 1985). Beryllium also has a stronger affinity for clay minerals than for organic matter, although beryllium binds more strongly with soil fulvic acids at higher pH (Esteves & Machado, 1996). Beryllium should be strongly adsorbed in most soils because it displaces divalent cations which share common sorption sites (Fishbein, 1981).

Beryllium is chemically similar to aluminium, and, therefore, may be expected to adsorb onto clay surfaces at low pHs, and may remain precipitated as insoluble complexes at higher pH (Callahan et al., 1979). As a result, beryllium would be expected to have limited mobility in soils (ATSDR, 1993) and mud residue from Bayer refineries.
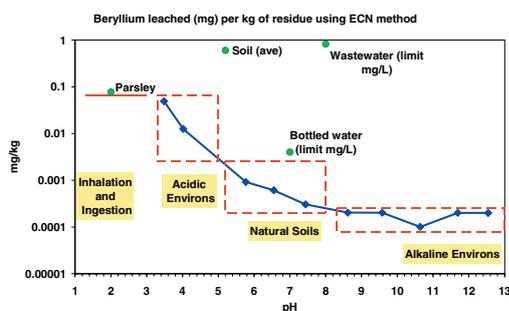
Figure 5. Leach results for beryllium from mud residue (log scale) at different pH. The relevance of the different pH regions to the environment is indicated, as are some example spot concentrations and USEPA limits for beryllium (as per ATSDR, 2002).

The latter expectation is supported by preliminary leaching data. For these tests sub-samples of residue are held in contact with solutions of various pH then the concentrations of beryllium in the leachate solutions are analysed after a specified holding time that enables a steady state to be reached. The methodology known as the "pH dependence test" is described in more detail elsewhere (Carter et al, 2005).

A plot of the data (Figure 5) shows that between pH 6-13 there is negligible effect from pH on the mobility of beryllium. The mobility is slightly greater at pH 2-4, however even under these conditions the leached amounts are extremely small.

7   Summary and recommendations

For researchers familiar with aluminium chemistry the similarity of beryllium and aluminium provides some advantages when gathering information, establishing analytical methods and proposing hypotheses.

However the similarity also means that the separation of aluminium and beryllium, especially within Bayer process constraints, is extremely challenging. It also complicates the establishment of proofs for hypotheses. To make matters more difficult a reliable method for the direct identification of beryllium *species* at trace concentrations in Bayer samples is yet to be developed.

In summary, beryllium is a potential issue for smelters that may be able to be addressed at the source (the refineries). Further work is required to determine if a viable process can be established.

Acknowledgements

References

Agency for Toxic Substances and Disease Registry (ATSDR), 2002. Toxicological profile for beryllium. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service. Atlanta, GA

Agency for Toxic Substances and Disease Registry (ATSDR). 1993. Toxicological Profile for Beryllium. U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, Atlanta, GA.

Alderighi, M. Gans, S. Midollini and A. Vacca, Aqueous Solution Chemistry of Beryllium. Adv. Inorg. Chem., 2000, 50, 109-172.

Bardossy, Gyorgy, 1982, Karst bauxites, bauxite deposits on carbonate rocks, in Developments in economic geology 14: Amsterdam, Elsevier, p441

Bear, I,J; Turnbull, A, G, 1965 The Heats of Formation of Beryllium Compounds. I. Beryllium Hydroxides. J. Phys. Chem., , 69, 2828-2833.

Beus, A.A. 1966. Distribution of beryllium in granites. Geochemistry, (USSR). 5: 432.

Bowen, H. J. M., 1979. Environmental chemistry of the elements. New York, NY, Academic Press.

Callahan MA, Slimak MW, Gabel NW, May IP, Fowler CF, Freed JR, Jennings P, Durfee RL, Whitmore FC, Maestri B, Mabey WR, Holt BR, Gould C 1979 Water-related environmental fate of 129 priority pollutants. Washington, DC, US Environmental Protection Agency (EPA-440/4 79-029a).

Carter C. M., Cooling D., Matheson T., van der Sloot H. A., van Zomeren A. 2005 New approach to leach testing of bauxite residue to support management decisions in view of beneficial application and storage, Paper submitted for AQW, Perth 2005.

Darwin. G.E, Buddery. J.H, 1960, Metallurgy of the rarer metals – 7 Beryllium,. Butterworths,. London.

Deubner, D; Kelsh, M; Shum, M, Maier, L; Kent, M; Lau, E; 2001, Beryllium Sensitization, Chronic Beryllium Disease, and Exposures at a Beryllium Mining and Extraction Facility, Applied Occupational and Environmental Hygiene, Volume 16(5): 579–592, 2001

Esteves, Da Silva JCG, Machado AASC. 1996. Quantitative study of Be(ii) complexation by soil fulvic acids by molecular fluorescence spectroscopy. Environ Sci Technol 30(11):3155-3160.

Fishbein L. 1981. Sources, transport and alterations of metal compounds: An overview. I. Arsenic, Beryllium, Cadmium, Chromium, and Nickel. Environ Health Perspect 40:43-64.

Grew, E.S. (ed.), 2002. Beryllium: Mineralogy, Petrology, and Geochemistry. Reviews in Mineralogy & Geochemistry, vol. 50.Mineralogical Society of America, p691.

Grocott, S C. 1988 Bayer liquor impurities: measurement of organic carbon, oxalate and carbonate extraction from bauxite digestion. Boxall, L G. Light Metals 1988; 1988 Jan 25-1988 Jan 28; Phoenix, Arizona. Pennsylvania: Metallurgical Society; c1987: 833-841. 926ISBN: 0-87339-031-8.

Hostache, G; Guittard, S; Eyraud, C, 1968 Growth and Evolution of Crystallites of Beryllium Hydroxide in Solutions of Sodium Beryllate. Analogy with Aluminium Hydroxides. Bull. Soc. Chim. Fr., 1851-1855.

Lambert, I; Clever, H.L. 1992 Alkaline Earth Hydroxides Water Aqueous Solutions. Solubility Data. Beryllium Hydroxide-Water Systems. Solubility Data Series, 52, 2-48.

Lewis, R.A. 1948, Reaction of BeO with molten Na3AlF6-CaF2-Al2O3 Compositions, Alcoa Internal Report

Lum KR, Gammon KL. 1985. Geochemical availability of some trace and major elements in surficial sediments of the Detroit River and western Lake Erie. J Great Lakes Res 11:328-338.

Navrátil, T., Skrivan, P., Minarik, L., Žigová, A 2002 Beryllium Geochemistry in the Lesni Potok Catchment (Czech Republic), 7 Years of Systematic Study, Aquatic Geochemistry 8: 121–134.

Patnaik, Pradyot, 2003 Handbook of Inorganic chemicals, McGraw-Hill, ISBN 0-07-049439-8,p99

Reeves, A. L. 1986, Beryllium. In: Handbook on the toxicology of metals, Vol. II., 2nd Edition. New York, Elsevier Science Publishing Co., Inc., pp. 95-116.

Schmidbaur, H, 2001, Recent Contributions to the Aqueous Coordination Chemistry of Beryllium. Coord. Chem. Rev., 215, 223-242.

Stern, R.A., Griffin, B.J., Clode, P.L. and McNaughton, N. 2004, "Sub-micron ion probe technology arrives in Australia, opening new research opportunities in the chemistry and isotopic properties of materials, minerals, and biological samples." Proceedings of the 18th Australian Conference of Microscopy and Microanalysis, ACMM-18. Geelong, Australia. 2nd – 6th February 2004. pp39

Vaessen H, Szteke B. 2000. Beryllium in food and drinking water- a summary of available knowledge. Food Additives and Contaminants. 17(2):149-159.