

## BERYLLIUM IN POT ROOM BATH

Stephen J. Lindsay<sup>1</sup>, Dr. Charles L. Dobbs<sup>2</sup><sup>1</sup>Alcoa Inc.; Primary Metals; 300 N. Hall Rd. MS-01, Alcoa, Tennessee, 37701-2516, USA<sup>2</sup>Alcoa Inc.; Alcoa Technical Center; 100 Technical Drive, Alcoa Center, Pennsylvania, 15069, USA

Keywords: Beryllium, Beryllium Fluoride, Beryllium Difluoride, Sodium Fluoroberyllate, Pot Bath, Concentration, Dilution

## Abstract

Concentrations of beryllium in pot room bath have become a multi-national issue of concern in recent years. In this paper the authors discuss the mass flow mechanisms that permit beryllium to become concentrated in pot bath as well as those factors that limit the reduction of beryllium concentration when the source of contamination is removed. Some general guidelines are proposed regarding decay rates in pot room bath.

## Introduction

Concerns about worker exposure to materials that contain beryllium, Be, or beryllium compounds have grown substantially in recent years. Industrial health efforts have been primarily focused on the exposure of workers to Be in metal working or welding. Some attention has been turned to the aluminum industry and to pot room operations in particular due to the observation that Be concentrations in smelter bath can be elevated. However, not much is known or has been published on the nature of beryllium in pot room bath. What is commonly known is that it appears to concentrate more in some smelter operations than in others and that it takes years for concentrations to decay once the source of Be is removed.

The ability of beryllium to concentrate in pot room bath is not surprising. In the Periodic Table Be is located near lithium, sodium, magnesium and calcium and is a Group 2 metal. Beryllium is an alkaline earth metal, many compounds of which are toxic. Discovery of the element in the mineral beryl, was reported by Nicolas Louis Vauquelin in 1789. Beryllium metal was isolated by Wöhler and Bussy in 1828. Group 1 and 2 metals (e.g. lithium, sodium, magnesium, and calcium) readily form fluorides in pot bath and all have very low partition coefficients with the product metal. The loss rates of Be to bath and metal production limit its concentration in typical potroom bath.

Beryllium is lost to a number of sinks including the cathode, dust losses and especially to pot bath that exits the smelter. The science is not as complex as the details of the overall mass balance can be. Understanding the loss mechanisms primarily boils down to having a good understanding of the sodium mass balance. Some generalities can be derived from such analysis that can also serve as general guidelines for those concerned with Be in pot bath. This paper is aimed at these generalities and building upon common understanding of the Be mass balance for pot room bath.

## Discussion – Beryllium Inputs

Beryllium may enter the pot room bath from many potential sources. Alumina, coke, pitch, aluminum fluoride, cryolite, purchased bath, cathode materials and others have the potential to

place beryllium in contact with pot room bath where it dissolves to form Be ions. These combine to form compounds such as beryllium fluoride, also known as beryllium difluoride,  $\text{BeF}_2$ , and sodium fluoroberyllate,  $\text{Na}_2\text{BeF}_4$ , a material that is not dissimilar to atomlite (its aluminum analog). The most common sources of Be are fresh alumina, and pot room bath that has come from another smelting location.

Although beryllium may be reported as  $\text{BeO}$  in raw materials the convention is to refer to the quantity of Be, rather than  $\text{BeO}$ , that is in material inputs, pot room bath or metal.

“The source of beryllium in alumina is trace levels present in some bauxite deposits.” [1] The mineral beryl,  $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ , is an alumino-silicate like many other impurities that are found in bauxite. The form of beryllium in bauxite is not known and is probably a combination of minerals like beryl, bertrandite, chrysoberyl, etc.

In smelting grade alumina, SGA, the concentration of  $\text{BeO}$ , expressed as the oxide, can vary from non-detectable to as much as 20 ppm which is roughly equivalent to 7 ppm of Be. There is no commercially available method to remove low levels of beryllium from either bauxite or SGA. The level in alumina is controlled by the source of the bauxite.

Typical levels of Be in alumina are not of particular concern for the SGA itself since it is so dilute. However, due to the large amounts of alumina that pass through a smelter, and the nature of Be to concentrate in pot bath, SGA is quite often by far the major input stream of beryllium into a smelter.

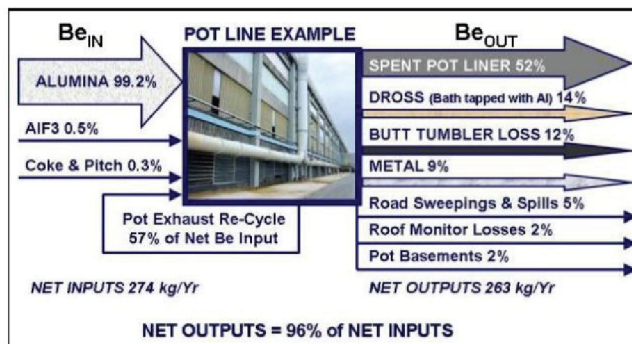


Figure 1 – Actual Beryllium Mass Balance Example

Coke, pitch, AIF<sub>3</sub> and anthracite are also derived from materials taken from nature. While the input levels of Be from these products is typically very low or non-detectable, trace levels may be found that vary with the sources of crude oil, fluorspar, hydrate and/or coal. In cases where smelters have extremely low levels of Be in alumina the input from all sources will typically generate an

equilibrium concentration of less than 10 ppm in pot bath. In cases where the major source of Be is alumina, the combined total of AlF<sub>3</sub>, coke, pitch and cathodes typically contribute less than 1% of the total input of Be to the smelter as in figure #1.

The other common source of Be to smelters is pot bath that has been purchased or transferred from a smelter that has used a raw material source containing beryllium. Since Be is concentrated in pot bath the transference of many tons can bring with it a substantial amount of Be that is generally in the form of beryllium fluorides. In some cases this transfer mechanism has been known to raise the average Be concentration to 70 ppm in liquid bath.

**Discussion – Beryllium Concentration**

As with some other metallic oxides BeO is miscible in Na<sub>3</sub>AlF<sub>6</sub> and as with other alkaline earth metals such as Na, Li, Mg and Ca, Be will tend to stay in the bath and combine with fluoride rather than report to the metal. These Group 1 and Group 2 elements have very low partition coefficients due to their strong affinity to halogens such as fluorine. Thus only a small amount of Be will be found in aluminum production. Locations that have in excess of 150 ppm of Be in pot room bath will have less than 1 ppm of Be in the product metal.

Without other sinks for beryllium beyond the small amount that leaves with metal production it concentrates in the pot bath until the mass of Be<sub>IN</sub> at low concentrations in alumina approximates the mass of Be<sub>OUT</sub> in pot bath at high concentrations. One estimate indicates that Be would concentrate to levels greater than 2500 ppm in bath if metal were the only avenue to exit the system. This is on the order of 500 to 1000 times the concentration of an SGA that is considered to be relatively high in Be content. At steady-state the actual concentration of Be in pot bath is on the order of 40 to 90 times that of fresh SGA, with 60X being most typical.

While beryllium concentrates to approximately sixty times that of fresh alumina in liquid bath limited data indicates that it does not concentrate uniformly in all forms of bath. Bath in anode cover, also known as crust bath, will have beryllium concentrations that range from the proportion of bath that is mixed with alumina to as much as one half to a full order of magnitude greater than the concentration of Be in liquid bath. See figure #2.

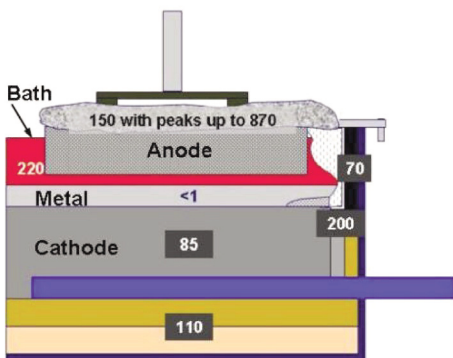


Figure 2 – Beryllium Concentration Examples

The mechanism that drives concentration of Be within the layer of anode crust also drives a similar phenomenon in the cathode. The hottest regions of the cathode will have relatively uniform concentrations of beryllium. Regions near the freeze isotherms can have Be concentrations that are three times greater than those of the hot zones. Colder zones of the cathode that are well beyond the freeze isotherms have very low concentrations of beryllium. This is shown in figure #3 below.

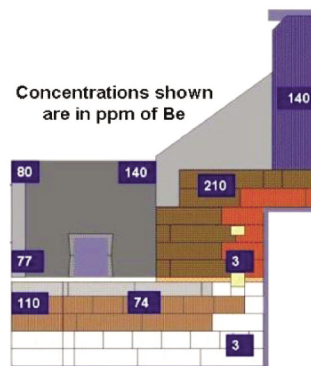


Figure 3 – Beryllium concentrations in cathodes

The vapor pressure of beryllium fluoride compounds and heat are both contributing factors that are suspected of being of primary importance to this phenomenon. This may be related to the vapor pressure of BeF<sub>2</sub>, melting point 544°C, sublimation at 800°C [2] and migration or deposition of BeF<sub>2</sub> and Na<sub>2</sub>BeF<sub>4</sub> within the layer of crust bath and within the cathode along isotherm lines.

**Discussion – Beryllium Outputs**

Aside from carbon dioxide, metal production accounts for the largest output by weight from reduction cells. But with very low concentrations of Be, aluminum falls far from accounting for the bulk of beryllium lost from the cell. However, metal production does carry away 5% to 10% of total Be input and thus accounts for a significant fraction of Be losses.

Other potential sinks are relatively small in terms of annual tonnage when compared to metal production. For Be<sub>IN</sub> to equal Be<sub>OUT</sub> this implies that at least one exit stream will have a Be concentration and mass loss that is relatively high.

This does not imply that all sinks are highly concentrated with beryllium compounds. Secondary alumina has concentrations of Be that are higher than that of fresh alumina, but much lower than that of bath and other materials. Dust losses of secondary alumina will therefore be only a minor sink for beryllium.

To understand the various exit streams for Be one should follow the paths of two other elements. The first is sodium in every form of bath exiting the smelter. The second element to follow is the fluorine that Be is so highly attracted to.

The sum of bath losses including that to cathodes will always account for the bulk of beryllium that exits any smelter. However, this involves many small and varied streams. An obvious stream to consider is that of excess tapped bath that may be crushed and sold or transferred to other smelters. Tonnages

may be relatively small, but with high concentrations a significant portion of the Be mass can flow to this exit stream, often in the range of 5 to 15% of total beryllium input.

Using a hypothetical example consider a smelter that produces just over 208,300 mt of aluminum per year. This location consumes 400,000 mt of alumina per year with a reported BeO equivalent of 8.3 ppm or 3.0 ppm of Be. There are no other significant inputs of Be to this smelter. Thus approximately 1200 kg of Be will enter this facility each year. If the concentration of Be in pot bath is 180 ppm and the plant generates 50 mt of excess bath for sale or transfer each month then roughly 108 kg or 9% of the net Be input leaves with the excess bath stream.

Closing this fraction of the Be mass flow loop helps to understand the bigger picture of beryllium losses to bath streams. Investigation into how much bath is lost each year to other streams will naturally follow in any undertaking to develop a complete mass balance. These streams will include; dust losses, dross leaving the ingot plant, accumulations of excess bath in piles, storage, material under pots, and other losses.

The key to understanding the many individual bath streams is to have good knowledge of the sodium balance for the smelter overall. It may be a surprising statistic but many smelters receive enough sodium and fluoride each year to displace between 33% and 50% of the total bath inventory. Most who work with plant operations do not realize that this much bath turns over each year. This is so since the flows of sodium are insidious rather than obvious.

Let's take a closer look at this claim using our hypothetical smelting example. There are a total of 468 pots operating at 160 kA in this smelter. The total bath inventory including liquid, solid, in anode cover and in all forms of storage is 10,250 mt, or about 20 mt/pot plus 10% in inventory.

The Na<sub>2</sub>O content of the alumina to this smelter is a fairly typical 0.41%. Some of this goes to sodium intercalation in cathodes and some to other sinks, but if all went to pot bath it would generate 4,200 mt each year.

Consumption of soda ash is relatively high at this smelter at 0.60 kg/mt Al. If all of the sodium in this stream went to make bath it would generate 190 mt of bath each year.

This smelter also consumes 30 mt of cryolite each month to support new pot starts. This stream will generate an additional 410 mt of bath each year.

In all this smelter brings in enough sodium each year to displace 47% of the average bath inventory, or 4800 mt.

A quick look at AlF<sub>3</sub> consumption confirms the magnitude of these calculations. Our example smelter consumes 19 kg AlF<sub>3</sub>/mt Al produced, or 3960 mt/yr. Enough to make 4830 mt of bath if all of it went to this sink.

These calculations are not offered as precise mass balances for either sodium or fluoride. They only serve to illustrate the point that the mass balance for pot bath is highly dynamic and that a large fraction of the bath inventory in a smelter turns over in any given year.

This also supports the premise that the major sink for beryllium is pot room bath loss in its various forms. Thus, net inputs of Be are primarily counter-balanced by steady dilution of pot room bath. While there are faults with these over-simplified calculations, consider one additional Be metric from our example smelter. If 1200 kg of Be enters this example smelter each year and 4800 mt of bath at 180 ppm were to leave it implies that 864 kg of Be, 72% of the input, leaves with the bath in one form or another. The balance leaves with metal, secondary alumina dust and fume, carbon dust skimmings, in forms of bath in that have higher Be concentration than tapped bath, and even a little concentrated in any hard gray scale that is accumulated and eventually discarded.

Since not all incoming sodium goes to make new pot bath with the proper amount of excess fluoride it is necessary to understand where the Na goes.

Some is accumulated and then held, sold or transferred as was illustrated in the example in which 9% of the net Be<sub>IN</sub> was accounted for via bath sales. Accounting for the beryllium in this particular stream is relatively easy to do.

Much sodium and basic bath permeates the cathodes via ingress and intercalation. Following the beryllium mass flow here is not so straightforward. Since the dry weight of new vs. consumed cathodes generally increases by 30% to 50% we might expect that the average Be concentration in spent pot lining should be between 40 and 60 ppm if it is 180 ppm in pot bath. This is well within the observed range for many pot types and is especially so for those pots which have been meticulously cross-sectioned with the samples kept dry. Note that since BeF<sub>2</sub> and Na<sub>2</sub>BeF<sub>4</sub> are quite soluble in water, spent pot liner that has come in contact with moisture will not yield accurate results for Be content.

Turning once again to our example smelter the pot life is 2000 days and spent pot liner generation is 33 kg/mt Al produced. If the average concentration of Be in the spent pot liner is 60 ppm then 413 kg/yr of Be leaves this way, 34% of the total Be<sub>IN</sub>.

Losses to spent pot liner, sales of excess bath and metal flow can bring our accounting for net Be losses up to >50% of the total Be<sub>IN</sub>. The remaining Be must be tracked down by looking at bath that exits with metal, bath losses at various concentrations, bath dust losses, carbon dust losses, pot fume losses and secondary alumina losses. A mass balance on Be may not close completely, but this may often be due to the lack of good information on exit streams. A thorough mass balance is best done during steady state conditions and should close such that net outputs are within 15% of net inputs.

#### Discussion – Disruption to Steady State

A valuable way to gain insight into the mechanisms of beryllium accumulation and decay is to gather and analyze data when changes occur that disrupt steady state conditions. Such case studies may be based upon the introduction of a new source of Be to the pot room bath or the elimination of a source of Be with a change in raw materials.

Increases in Be concentration are relatively simple to model when a new source is added so long as the concentration of Be or beryllium mineral in the source has been accurately determined. An initial spike in beryllium concentration in the liquid bath is

expected, followed by some relatively rapid decay as Be migrates into the frozen forms of bath throughout the smelter. This period is followed by a slow, asymptotic period of decline.

An example is offered in figure #4. This smelting location had a background level of beryllium in pot room bath was relatively low, at 3.5 ppm. When a single shipment of a different alumina source was received it provided the opportunity to follow the event and confirm the prediction for the increase in Be concentration. Eventually this information and additional data led to the development of a simple algorithm to that is used for making predictions for Be concentrations in similar cases.

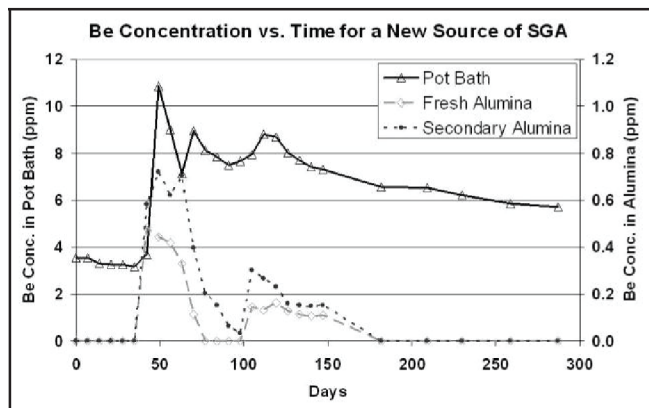


Figure 4 – Single Shipment Beryllium Accumulation and Decay

The algorithm is:  $Be_{PEAK} \text{ (ppm)} = Be_{INITIAL} \text{ (ppm)} + [Be_{IN} \text{ (kg)}/\text{Total Liquid Bath in Smelter (kg)} * 1,000,000/100 * \% \text{ of } Be_{IN} \text{ consumed in 25 days}]$

In this case  $Be_{IN}$  represents the total mass of beryllium in the alumina shipment. If it is consumed over more than a twenty-five day period then the input mass is limited only to the amount consumed during the first twenty-five days.

Another way to examine the dynamics of beryllium concentration in pot room bath is to examine what happens when a major source of Be contamination is suddenly removed. Figure #5 includes the decay trace that is shown in figure #4 after the shipment was consumed along with examples from six other locations that had initial concentrations of Be in bath ranging from 10 to 200 ppm.

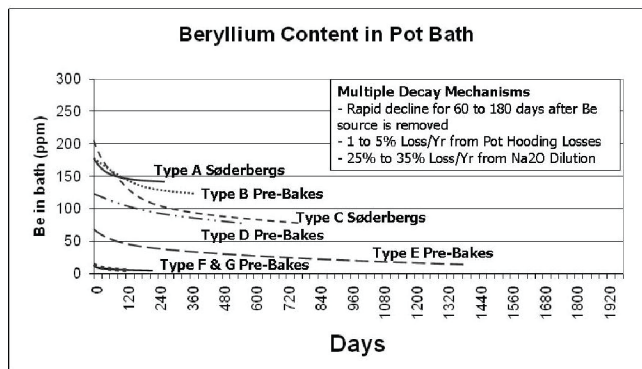


Figure 5 – Comparisons of Be Decay Rates in Tapped Bath

The examples in figure #5 all represent Be in tapped bath from both pre-bake and Soderberg pot types. Included are smelters that have used an individual shipment of alumina containing Be in concentrations over 1 ppm, smelters that have used alumina containing Be between 3 and 4 ppm for many years, and a smelter that had never used alumina containing beryllium, but that had used crushed tapped bath from a location that contained Be at concentrations greater than 200 ppm.

Although the circumstances are varied some generalities emerge when a major source of beryllium contamination is suddenly removed. There is a period of rapid decline of two to six months followed by a period of prolonged steady decline. The initial rapid rate of decline characterizes a shift from the Be input rate being a primary factor for determining the steady-state Be concentration in pot bath to Be dilution rates being the primary determining factor for residual concentrations in pot bath.

Note that there appear to be two main factors that determine the rate of change of Be concentration. The first can be called the “bath factor”, or the ratio of tons of bath to tons of alumina consumed. The second is the rate of sodium input to the smelter.

These two factors may be compared to a glass bowl full of colored water that has a clear dilution stream entering and causing the bowl to overflow to a drain. The “bath factor” is analogous to the size of the bowl and the sodium input is analogous to the flow rate of the dilution stream.

A smelter with a relatively small amount of bath per ton of alumina consumed will have a relatively rapid rate of decay in beryllium content. A small bowl will be diluted more quickly than a large bowl when both have equal overflow rates.

The initial rapid rate of decrease in Be concentration lasts two to six months while the system adjusts to the new balance between inputs and outputs. The ratio of tons of bath to tons of alumina consumed, or the size of the bowl, plays a large role in modeling this period of decay in beryllium concentration.

Smelters with a relatively high  $Na_2O$  content in alumina will have a more rapid rate of steady decline in Be concentration. This is like having a dilution stream with a relatively high flow rate. The point is illustrated in figure #6 where the average  $Na_2O$  content is compared to the prolonged decay rate of the curves shown in figure #5.

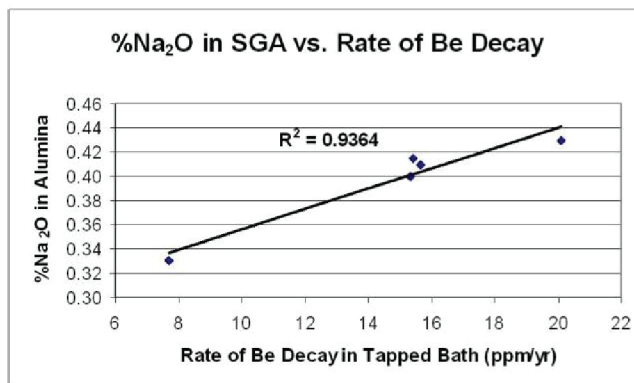


Figure 6 – Relation of  $\%Na_2O$  to Be Decay Rate



There are multiple sources of Na that contribute to the rate of dilution. Sodium input in alumina is typically the largest factor by far. The consumption rates of sodium carbonate or soda ash, cryolite and imported bath also play a role in dilution.

When these factors are combined a rough rule of thumb emerges. Six months after quitting a source of Be input the rate of decay of beryllium concentration in pot room bath will be 35% +/-5% per year. In other words if the Be concentration begins the year at 100 ppm it will drop to 65 +/-5 ppm at the end of the first year, 42 ppm at the end of the second year, 27 ppm at the end of the third year and so on. A more general rule might be that *one-third of the concentration of beryllium will be lost each year relative to the starting point for that year*. Of course this varies from case to case, but having such a general guideline is often useful.

A third factor, the ratio of bath in liquid form to bath in solid form is also suspected as being of importance to the initial rate of change of beryllium concentrations in tapped bath illustrated in figure # 5. This has to do with the concentrated levels of Be that can be found in crust bath and the concentrating effect that it may have on Be in liquid bath as it is consumed.

Consider one last time our hypothetical smelting example in which the liquid bath has an average Be concentration of 180 ppm. One ton of crust bath from this smelter has an average of 140 ppm Be and 33% alumina content. When this material is consumed to the pots the 0.67 tons of liquid bath that is generated will have the equivalent of 209 ppm of Be. A plant that has large reserves of crust bath is likely to decay at a slower initial rate than a plant with little inventory of crust, and basement, bath.

#### Other

Although it is open to further study high concentrations of beryllium have not been found in materials other than pot bath. Carbon dust may be an exception to this based upon limited evidence. It has been well documented in the literature that other contaminants such as Fe concentrate on carbon dust that floats on liquid bath. Beryllium may do likewise. This is only theory at this point and subject to further study.

The Be concentration of particulate material in the inlet ducts to dry scrubbers indicates that the Be concentration in bath determines the concentration in this material and thus in reacted or secondary alumina.

One other factor that is open to further investigation is treatment of beryllium laden bath with water. The beryllium found in SGA is essentially insoluble in water. However, in individual bath samples beryllium content may range from being nearly insoluble to as much as 95% soluble in water. Most samples are 50% to 90% water soluble. This property may open some avenues to beryllium extraction by giving pot bath a “bath” if the reader will excuse the expression. Of course this also begets the question of what to do with the beryllium fluoride once it is in wash water.

#### Conclusions

There are generally two common sources for beryllium accumulation in pot bath. The most common is Smelting Grade Alumina. The other primary source is via purchase of pot bath

from a smelter that has used alumina containing beryllium. In either example Be in alumina is a common root.

Beryllium is highly attracted to fluoride and has a low partition coefficient. Thus Be concentrates in pot bath in the range of 40X to 90X that of the concentration in incoming alumina. The most common concentration is 60X that of alumina, but this can vary based upon the rate of net sodium input and losses from a smelter.

Beryllium also tends to concentrate in what may be isotherms in both the pot crust and the spent pot lining. The melting point and vapor pressure of beryllium fluoride in combination with the temperature of molten pot bath are suspected as the driving forces of this phenomenon.

A small portion of beryllium is lost to the product metal. It is not uncommon for a smelter with 150 ppm of Be in pot bath to have less than 1 ppm of Be in metal. The primary sinks are with bath losses to cathodes and spent pot lining, bath transferred with metal that goes to dross, bath sales, spent anode cleaning residue, carbon dust skimmings and all other forms of bath losses. Following the losses of bath from a smelter is the key to understanding the losses of beryllium.

Changes in Be concentration in liquid bath can be readily modeled using data on a new raw material stream that contains Be.

Once beryllium is present in pot bath the primary mechanism to reduce its concentration once the input source has been removed is dilution and loss to the cathode which one might consider a form of dilution as the bath must be replenished. In general smelters bring in enough sodium in various forms to replace 33% and 50% of their total bath inventory each year. The amount of sodium entering and leaving a smelter is an important factor in determining how quickly beryllium concentration in pot bath can be reduced.

The other main factor in the determination of how quickly the beryllium concentration will change is the size of the “bowl” or the relative amount of bath that is kept in circuit per ton of alumina that is consumed. Those plants with greater economy of pot bath inventory will see more rapid increases or decreases in Be content when sources of Be are added or removed than those smelters that have relatively large reserves of pot bath kept in circuit. The inventory of various forms of solid bath relative to the total inventory of liquid bath may play a role in the dilution rate as well.

Six months following the termination of a raw material containing beryllium the concentration of Be in bath will decline by about one-third of the initial value of any given year.

Finally, there are factors about beryllium in pot room bath that require further study including mechanisms of how it concentrates in crust bath or on carbon dust and if its relatively high solubility in water may become an effective means at controlling the risks that may be associated with worker exposure.

#### References

1. Eyer, S. L., Nunes, M. D., Dobbs, C. L., Russo, A. V., Burke, K., “The Analysis of Beryllium in Bayer Solids and Liquids” ,

Proceedings of the 7<sup>th</sup> International Alumina Quality Workshop, 2005, pp 254 – 257

2. United Nations Environment Programme, the International Labour Organisation and the World Health Organization, International Programme on Chemical Safety, “Environmental Health Criteria 106 Beryllium”, Section 2.2, Table 3 Physical and chemical properties of beryllium and selected beryllium compounds

<http://www.inchem.org/documents/ehc/ehc/ehc106.htm>

#### **Acknowledgements**

Luca Bellan, Luciano Nalon, Moreno Niero, Roberto Nalesso, Lee Blayden, Mike Palazzolo and Programma Ambiente for assistance with sampling.

Greg Kraft and Giuliano Biasutto for sponsorship

Miland Chaubal, Sherwin Alumina Company, “Beryllium in Aluminum” Aluminum Association Be Task Group, August 2002

Merino, Dr. Margarita R. (Ph.D. – Florida State University) – for her encouragement, dedication and support