

Excess Bath Material - Sustainable Solutions to an Environmental Liability

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Abstract

The problem of excess bath material is a growing concern to the global aluminium smelting industry. Bath material (bath) is the electrolytic material used in the production process for primary aluminium. Bath is generated in-situ during the production of aluminium, where sodium compounds combine with the aluminium fluoride (AlF_3) added to reduce electrical energy requirements. The final mixture consists primarily of cryolite (Na_3AlF_6), excess aluminium fluoride, calcium fluoride (CaF_2), alumina (Al_2O_3) and other minor elements. The exact amount of excess bath generation varies with different raw materials used and depends on pot life. Under normal circumstances the excess generation far exceeds the consumption (e.g., in pot relining) of a smelter. Hence a typical smelter will produce a continuous surplus of bath for most of its lifetime. With the strong growth of the primary aluminium capacity over the past two decades, the amount of excess bath has increased dramatically, with demand, mainly coming from new smelters for their start-ups, being outstripped by the excess generation. This has created a problem for the industry as stocks increase and become burdensome - and potentially an environmental liability. This structural change in the over-supply of bath happened gradually over the past years and has so far received little attention. As the aluminium industry moves rapidly towards a more sustainable and greener future, the option of landfill or long-term storage becomes unacceptable in many regions. This paper gives a historical and future overview of the global situation of excess bath material and its key drivers. The team of authors consists of technical experts of the electrolysis process, aluminium industry experts and specialists who have developed bespoke solutions to remove, upcycle and repurpose this excess material.

Keywords: Aluminium electrolysis by-products, Sustainability of aluminium production, Bath material, Cryolite, Solution to growing bath inventories.

1. Introduction

Bath is a by-product of the aluminium electrolysis process. The generation of bath globally is growing much faster than its traditional consumption or recycling pathways can support, hence the excess. Furthermore, because it is a fluoride bearing compound, bath is an environmentally challenging material to handle due to its status as a marine pollutant, and is costly to landfill. This is a growing problem that the aluminium industry globally has paid little attention to. However, the traditional markets cannot absorb the continuously growing oversupply.

Bathco, a leading bath trader and processor has developed alternative and sustainable solutions to consume the excess bath, able to treat any bath material regardless of quality or location. These innovative and proprietary solutions would be able to process all existing Bath inventory.

2. Discussion

Bath has become a growing issue for the primary aluminium industry because its generation continues to grow rapidly in line with the global growth in aluminium production, and smelting performance improvements. However, the aluminium industry has not focused on finding a solution for it due to its low economic value.

2.1 Growth of Excess Bath

Today, most smelters generate excess bath. Historic literature suggests that the typical rate of generation was between 4.2 kg and 7 kg/t Al [1] but given today's predominant usage of graphitized cathodes, the typical net excess is now greater than 10 kg/t of aluminium produced.

Bath is the electrolyte used to dissolve alumina. There are a variety of qualities of bath, but a typical composition as marketed by Bathco is shown in the tables 1 and 2. Bath material is a by-product of the aluminium electrolysis process, the analysis is thus typical and based on composite sampling. Typical packaging size is 1-1.5 t in polypropylene big bags.

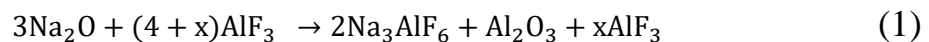
Table 1. Typical specification of chemical composition of commercial pure tapped bath material marketed by Bathco.

	Min (%)	Max (%)
Na ₃ AlF ₆	77	80
AlF ₃	11	14
Al ₂ O ₃	3	5
CaF ₂	4	5.5
Fe ₂ O ₃	<	0.05
SiO ₂	<	0.05
MgF ₂	<	0.02
P ₂ O ₅	<	0.02
C	<	0.15

Table 2. Typical bath size distribution, coarse grain size.

	Min (%)	Max (%)
0 – 20 mm	100	20
0 – 4 mm	40	60
0 – 1 mm	30	35

Bath consists primarily of up to 80 % cryolite. The generation and consumption of bath is therefore governed by the equation of cryolite generation, Equation (1):



The equation would shift to the right or the left depending on the sodium and aluminium fluoride balances maintained. These depend on smelter technology and operating conditions. The influencing factors are:

- A. Operating conditions as defined by cryolite ratio (NaF/AlF_3) or excess AlF_3 with the aim of operating at as low a temperature as possible. This is generally around 960°C or below than when lithium is used to the bath. Smelters do this to [2]:
 - i. Achieve highest possible current efficiency
 - ii. Maintain acceptable process window and as stable as possible pot operation
 - iii. Dissolve alumina efficiently, avoid anode effects and avoid sludge
 - iv. Achieve mass balance control with heat balance control and manage the interaction between the frozen ledge and anode cover material
 - v. Achieve adequate separation between liquid aluminium and liquid bath
- B. Sodium contained in smelter grade alumina (Na_2O) would shift the equation to the right thereby producing more bath. The scope for significant reduction of soda content in smelter grade alumina (SGA) is limited [3].
- C. Sodium losses into and through amorphous carbon cathode blocks would shift the equation to the left. However, the use of graphitized cathode blocks has reduced this sodium absorption mechanism and reduces sodium intake by a factor of 3, approximately, because of its pore structure.
- D. Some bath losses, traditionally occurred through poor hooding which contributed to lower net bath production, however with advances of scrubbing technology and hooding efficiency, as well as tighter environmental regulations, this ‘outlet’ for excess bath is being progressively reduced.
- E. Excess aluminium fluoride policy, which should range between 10 and 13 % though typically tapped bath contains 11-14 %. The higher the excess fluoride, the more the equation will shift to the right and produce more surplus bath.
- F. The authors believe that the use of inert anodes such as that featured by the ELYSISTM project would tend to produce more bath because of its narrow operating window at a lower temperature. There is limited public information on the subject but if the use of the inert anode technology were to become a norm, we foresee a significant additional increase in Bath generation

Advances in smelter technology over the years have shifted the sodium and fluoride balances in such a way that smelters have primarily become bath producers. The prevalent shift to graphitized cathodes and higher amperage cells in the smelting industry, combined with longer cathode life and better hooding efficiency, has resulted in an excess of bath production relative to its consumption. Hence, we have far more bath producing smelters than we do bath consuming ones. As such, the surplus bath, outside of China, is estimated to be above 200 000 t and growing. This stock equates to more than 3 years of the current annual consumption.

2.2 Excess Bath - an Environmental Liability

Bath is a useable by-product for which a market still exists. Yet, China has recently classified it into its “solid waste” category, and with this, banning any import into the single largest market for aluminium. While the authors of this article strongly disagree with the classification as waste, it highlights the need for an environmentally considerate handling of the excess bath.

It is worth noting Bathco's Material Safety Data Sheet (MSDS) on pure tapped bath material from 2016. It is clearly stated that bath must not be discharged into drains/surface waters/groundwater and must not be discharged into subsoil/soil. It also must carry a label for marine pollutant hazard. It is evident that bath must be considered an environmental liability. Moreover, an excessive generation of bath without a viable outlet increases the urgency of finding a sustainable solution.

3. Global Bath Balance – Past, Current and Outlook

3.1 Supply of Bath

a. Until the Year 2000 Excess Bath Was the Exception

The existence of excess bath material is closely linked with the conversion of pots from Soderberg paste technology to prebaked anode technology and the installation of gas scrubbing systems. When pots were not covered, and many Soderberg pots were in production, there was nearly no excess bath available. The smelters used synthetically produced cryolite to compensate for gaseous flux losses and for pot start-ups.

b. 2000 – 2018 Bath Market Starts to Form

With the shift to newer pot lining technologies of pre-baked carbon anode blocks and dry scrubbing systems, it also shifted the mass balance of sodium (lower net losses) in the aluminium production process resulting in a bath generation system, greater than required for internal consumption. Typical bath generation for pot lines with 100 kA-300 kA was about 4-5 kg/t Al produced. [1]

c. 2018 Onwards Excess Situation

In light of the advanced pot technology today with mostly graphitized cathode blocks and amperages of above 350 kA, the worldwide mass balance of sodium is shifting again and we are seeing a typical excess Bath generation of greater than 10 kg/t Al produced.

As an example of Bath generation; the volume of bath produced for a 500 000 t capacity smelter operating with industry standard technology and +350kA Amperage, would generate approximately 5 000 t of excess bath per year, possibly more, depending on the alumina content included in the bath.

3.2 Demand for Bath

a. Until the Year 2000 Steady Growth Phase

As per Figure 1, we saw a steady growth rate of aluminium production of about 100 % (from 10 million to approximately 24 million tonnes between 1973 and 2000), which was supported by the steady generation of excess bath.[4]

This phase particularly saw few aluminium smelters using bath for their start-up or the continuous production as they were used to consuming synthetic cryolite. Hence the demand for bath did not exceed surplus generation and at same time, stock levels of bath were at manageable levels.

b. 2000 – 2018 Accelerated Growth Phase

As per Figure 1, we saw an accelerated growth (of about 300 %) in aluminium production in the past two decades, especially in China, India and the Middle East.

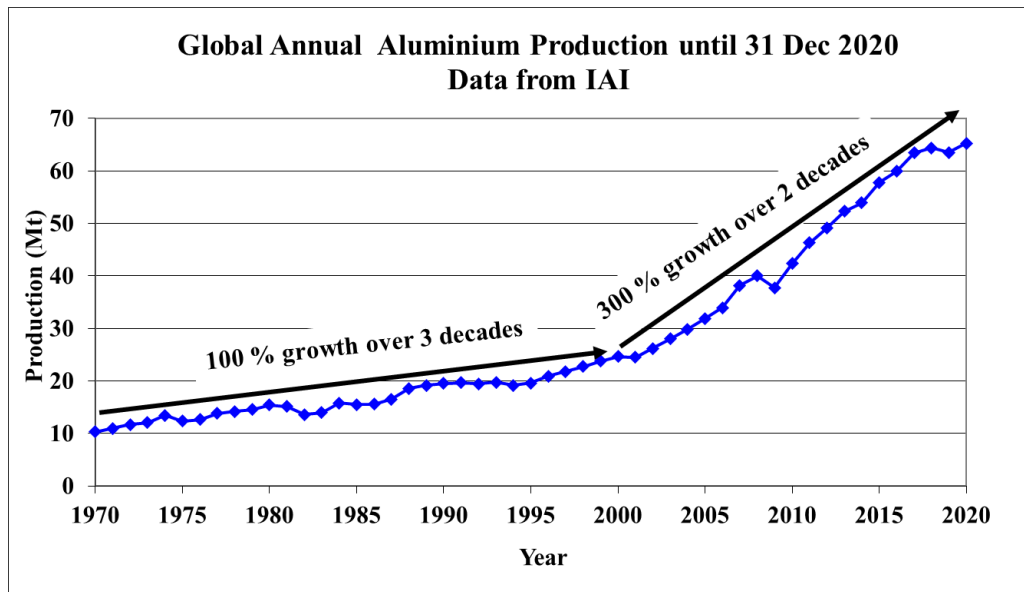


Figure 1. Global annual aluminium production in million tonnes, International Aluminium Institute data [4].

In this accelerated phase, the above-mentioned regions consumed about three quarters of the available Bath and at this point, did not yet have their own surplus. During this period, China shut down all its remaining - and bath consuming Soderberg smelters. With some regular tonnages of bath being available, it was possible for exchanges to be made between the producers and the consumers. Bath, predominantly being supplied by updated baked anode plants and being delivered to newly commissioned smelters for their initial start-up. During this phase, the authors also saw many of the western smelters changing their consumption pattern as they replaced a large portion of synthetic cryolite with bath for start-ups and continuous production, which further increased the demand for bath.

Hence, during this phase, the bath market remained fairly balanced with sizable demand coming mainly from the start-up projects (replacing synthetic cryolite) and stable bath generation coming from advanced technology smelters. Thus, due to this balanced supply-demand situation, all time high sales prices of bath were seen in this phase.

c. 2018 Onwards Estimated Growth

2018 was slower in terms of new capacities, but growth is widely expected to pick-up again from 2023 onwards. The growth rate for aluminium demand (primary and secondary) for the next 30 years (until 2050) is projected at rate of 4.2 % (Source: CM Group, IAI) [5]. This will provide a limited demand for bath, however, demand from new smelters for their start-ups is one-off, irregular and insufficient in quantity. Hence even with a pick-up in start-up activity, generation far outstrips forecasted demand. The authors expect that the few regular consumers left will likely convert to more modern technologies and stop consuming (and start generating surplus).

China stopped accepting imports of bath due to large domestic surpluses of bath. It is however likely that China will soon start exporting bath. The transition to fully graphitized cathodes – which absorb less Na – will lead to considerably higher rates of excess bath generation in modern smelters.

d. Oversupply

With the bath market being in balance up until 2018, the quality of tapped bath was diverse. Now, with the excess generation (oversupply) of bath in recent years, the preference of taking “premium” quality material (with a maximum 5 % Al_2O_3) has been observed. This contributes to the issue of surplus inventory of bath, with smelters having few alternatives but to store either on or/ off site at extra costs. Plus, those materials that cannot be sold or marketed due to quality concerns, would have no other use but to landfill, which in most countries is already a very expensive option mainly due to the hazardous nature of the material.

4. Different Streams of Bath Material in Aluminium Smelters

Depending on the exact processes in a smelter, excess bath can originate from a variety of processes. The most obvious – and qualitatively purest – is the tapping from running pots to maintain desired flux height. Aside from this, bath comes from cleaning the anode butts, cleaning tapping ladles, from shutdown pots, and from the basement, where it accumulates by falling through the floor grids.

Each stream of bath generates its own quality properties, in chemistry and granulometry. And not all smelters have an excess of each stream. In fact, many smelters recycle all or most of the streams by feeding the material back as an anode cover material. However, some smelters would, for example to maintain highest metal quality, not recycle all bath and instead choose to have different streams as excess. There are certainly arguments to be made both for and against this practice. At least until recently, bath with higher-than-normal contamination was very difficult to sell. Hence it was either put to landfill or stockpiled. In some cases, to the extent of tens of thousands of tonnes.

In terms of economics, one important aspect to be considered, is that the net excess of those bath-like materials will increase with a higher alumina content. For example, bath material collected from the basement often contains up to 50 % alumina. Not recycling this material inhouse, means essentially to add almost 50 % of additional material on top of the generated bath that is being disposed of.

Solutions are now available for all streams of bath – all qualities, including material that is contaminated with high alumina, high silicon and/or iron, and carbon. This is specifically interesting for smelters, that for process related or metal quality reasons, choose not to recycle low quality bath. For smelters that are able and willing to recycle, it may still be the most financially attractive option as it leads to an overall lower excess bath production and provides one stream of high-quality pure bath.

5. Solutions for Excess Bath

Excess bath issues have received little attention from the aluminium industry. Some of the reasons are that some smelters have in-smelter storage or access to external safe storage areas. Also, in the past, when the market was more balanced, there were enough sales opportunities, direct or via traders who secured an outlet for it. It is evident that the amount of bath being generated is far larger than the amount for which outlets can be secured by traditional consumers; those using it to start up new pots. Hence alternative applications and usages must be found. However, there are some limiting factors or challenges which are applicable in doing so.

5.1 Avoidance of Leaching

Bath material as well as its derivatives such as cover- or basement material contain fluoride salts. These are potentially leachable and therefore considered as a marine pollutant hazard, which must be avoided or at best eliminated. This could be achieved by encapsulating the fluoride compound in its final state in a sparsely leachable solid, thereby isolating it and eliminating the risk of fluoride bearing compounds to leach into groundwater.

Transferring bath material into a non-leachable solid state for safe disposal is quite demanding and costly when intended for disposal. It is environmentally and economically more efficient to upcycle bath material into a product that is consumed in applications where it is converted into a non-leachable solid.

5.2 Processing and Up-Cycling of Bath

One of the biggest challenges in many projects in the search of uses for bath material is the homogeneity of input material. Bath material can cover a wide range (tolerance) in its specification or can change over time, making it difficult or non-workable for certain processes. Furthermore, processes requiring narrow quality tolerances of the input material would only make use of a very small portion of the available bath. Refining such material to a homogenous product with workable narrow tolerances would add significant costs resulting in a product which might be workable, but commercially not feasible.

On the commercial side the challenge is that many potential processes require heavy investments. Given the low volume of narrow tolerance material, any investment in the solution would not be justified. Having one central processing centre leads to additional and substantial transport costs to the material brought in for processing, as well as generating unnecessary CO₂ emissions. A feasible way that has proved economically viable and more environmentally sustainable, is having decentralized, mid-sized processing facilities in close proximity to a cluster of smelters.

6. The Sustainable Path Forward

The need for finding a solution to the ever-growing excess bath problem has rested on trading companies such as Bathco for which bath processing, sale and trading is their primary business. Innovative solutions developed by Bathco will consume the existing stock of excess bath and would process future excess Bath generated by smelters. Hence a necessary step was moving from a traditional trading model, through substantial investments in R&D as well as developing processing techniques, to establishing bespoke solutions. One other key aspect is that users of upcycled products containing Bath material are typically consuming between 150 t – 300 t per year resulting in a large number of outlets which each need to be acquired, supplied and provided with a high level of customer service.

7. Description of Bathco Solutions for Excess Bath

Key features of the solutions follow:

- Sustainable regardless of the quality or composition of bath
- Compliant with environmental and safety regulations
- Decentralized processing facilities around the world for CF-reduction and efficient transport/logistics
- Controlled cradle-to-cradle process resulting in an encapsulated non-leachable solid, thereby rendering bath material non-hazardous

- In a stabilised form, this could be disposed of in an industrial waste landfill at minimal cost should there be a need to do so
- Upcycled into other industrial uses, lowering overall carbon footprint

8. Conclusions

Over the years, the primary aluminium industry has outgrown its own solution for the excess bath material it produces. The existing previous paradigm solution cannot absorb the industry's growing output and hence the situation has shifted from one of bath material balance being in equilibrium to a one where there is a clear supply excess. Therefore, new solutions were urgently needed.

This paper reports that, over the past decade, Bathco has developed several applications in various industries leading to effective and sustainable solutions for the excess bath issue. Bath material, regardless of quality, quantity, and classification, will be fully upcycled under total compliance with environmental regulations.

Bathco is currently putting in place additional capacity to be able to consume the increasing generation of bath and start reducing stocks of bath material. Bathco has set its clear goal to be the market leader in providing best possible and carbon neutral solutions to the excess bath challenge. With a global network of processing facilities, direct smelter contacts and centralised logistical operations team, Bathco manages transportation and handling of materials seamlessly with smelter operations.

9. References

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