A Low Cost, Sustainable Source of Alumina for Thermal Insulation

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In recent years non-energy raw material markets have seen major shifts in supply and demand patterns combined with short-term shocks. This commercial environment motivated the EU to launch a Raw Material Strategy ensuring the continued availability of essential inputs for European industry.[1]
The present situation has highlighted the need for "home-grown" alternatives to globally traded minerals. In particular, recycling as a source of value-added secondary materials, is becoming increasingly important. *RVA*, a company in north eastern France, produces not just one but three recycled material streams, one metallic and two mineral-based. One of the outputs, Valoxy®, is a low cost, sustainable source of alumina for thermal insulation and other non-metallurgical applications. Substituting Valoxy® for alumina can significantly reduce raw material costs. Furthermore, being derived from an established recycling process, RVA's recycled materials offer supply and price stability – a sharp contrast to virgin material extracted from nature.

1 An essential environmental service

RVA provides a critical environmental service to the aluminium smelters of western Europe. In the aluminium refining process, scrap is melted in rotary or reverbatory furnaces under a bath of molten salt, which floats on the metal surface.
The salt is typically a eutectic or near-eutectic mixture of sodium and potassium chlorides containing low levels of fluorides (cryolite). Molten metallic aluminium and its salt cover are successively tapped from the rotary drum surface.
The last salt mix tapped from the furnace contains residual aluminium metal (around 5 %) and various metal oxides, mainly aluminium oxide. This mixture solidifies in pans to become what is termed "salt slag". The molten salt layer performs two main functions:

- salt coats the metallic aluminium in the melt phase hence minimizing oxidation losses.
- fluoride in the salt facilitates break-down of prior oxide layers on the surface of the scrap and thence promotes improved separation between the aluminium and non-metallic contaminants.

At the end of the melt cycle the salt layer is tapped off and, on cooling, solidifies into a salt slag. This salt slag is a hazardous waste, which must be disposed of under controlled conditions. Historically, in Europe, aluminium salt slag was landfilled. More recently, a combination of tighter environmental regulation and high landfill costs has terminated this practice. Instead, aluminium salt slag is recycled in dedicated plants such as RVA. Reprocessing is recognised across the EU as the best practicable environmental option for salt slags. By contrast, the United States has yet unequivocally to mandate the processing of salt slags. As a consequence, landfilling of salt slags is still widespread. The interesting feature from a European perspective is that, with appropriate re-processing, salt slag is actually a source of essential raw materials.
Thus, RVA is playing its part to mitigate the supply pressures worrying the EU.

2 From waste to valuable raw materials

Three material streams are reclaimed from salt slag in the RVA process.

- Aluminium oxide-based material with the trade name, Valoxy®. Valoxy® comprises around 70 % alumina by weight and is offered as an effective, sustainable, low cost source of alumina for non-metallurgical applications including thermal insulation.
- Aluminium metal in the form of granules. This is returned to the refiners where it is melted as part of a scrap mix.
- A salt mixture comprising NaCl, KCl and CaF_2. This material is also returned to the refiners for re-use as the salt layer in the aluminium melting cycle.

All three streams are therefore returned to productive use in a double loop recycling process (Fig. 1).

3 The market for salt slag treatment

Since secondary aluminium production is largely dependent on molten salt, global

[1] Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions tackling the Challenges in Commodity Markets and on Raw Materials, February 2011

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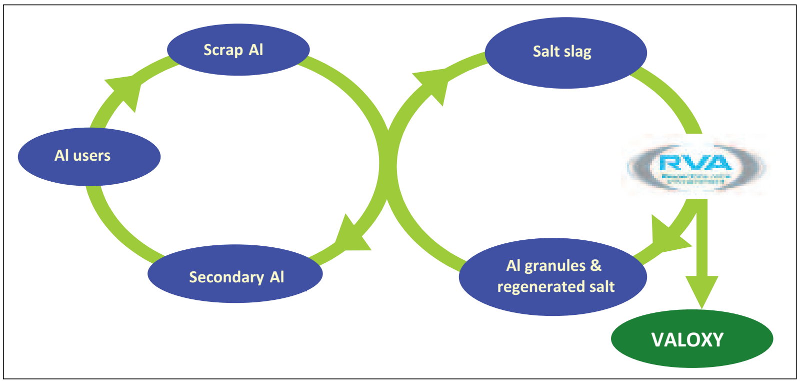

Fig. 1 Material flows from salt slag to value-added raw materials

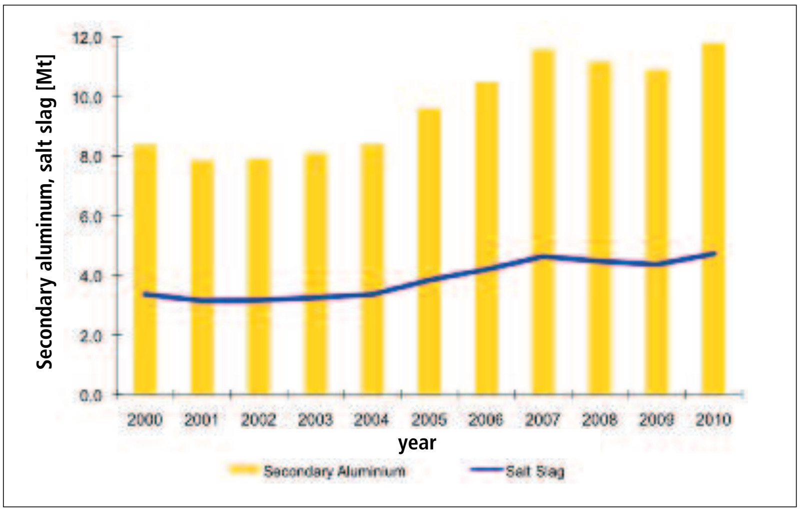

Fig. 2 World arisings of salt slag – a function of secondary aluminium production

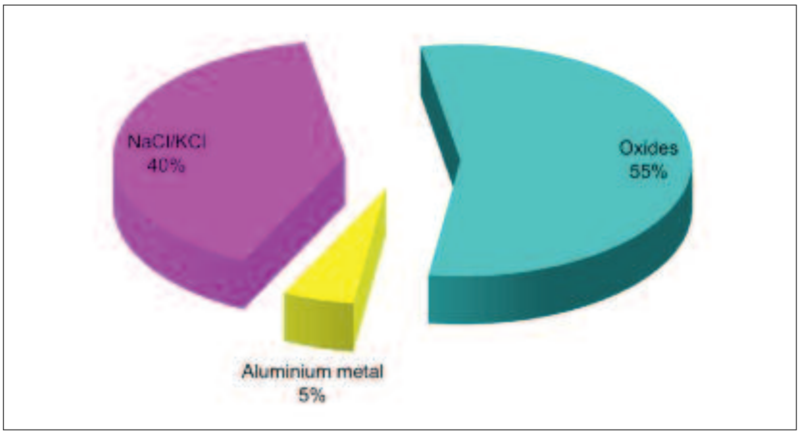

Fig. 3 Typical composition of salt slag

arisings of salt slag closely follow output from that industry. Between 300–800 kg of salt slag are produced for every tonne of secondary aluminium alloy. In 2011 worldwide secondary aluminium production stood at around 12 Mt. Taking a conservative figure of 400 kg slag/t aluminium, salt slag arisings may be estimated at 4,8 Mt worldwide (Fig. 2). The distribution of salt slags around the world follows the distribution of secondary aluminium production. This means around a million tonnes of slag are generated annually in Europe, 1,3 Mt in the US and China, now the dominant player, currently generating an estimated 1,7 Mt of salt slag p.a.

4 Salt slag and the global potential for secondary alumina

Around 40 % of salt slag by weight is the original salt mix used in the melting process. A further 5 % is aluminium metal in granular form. The balance is the oxide material from which RVA's secondary alumina, Valoxy®, is derived (Fig. 3).

Thus, the production of one tonne of aluminium alloy generates around 400 kg of salt slag which in turn can be used to produce 220 kg of secondary alumina such as Valoxy®. The global potential output of secondary aluminas can therefore be estimated at around 2,6 Mt per annum (Fig. 4). However, this material is not immediately available worldwide. The production of secondary aluminas, such as RVA's Valoxy®, unlike primary materials, is driven by two factors:

- a regulatory environment that prohibits landfilling of salt slags and mandates their reprocessing into useful products
- product and market development of secondary aluminas which enables their inherent economic value to be maximized.

Prohibition of landfilling salt slags is very advanced in Europe allowing companies such as RVA to offer a critical service using their slag reclamation technology.

As environmental regulations tighten in the US and also China, new slag recycling plants are likely to come on stream bringing with them a new secondary source of bauxite/alumina-type material. Utilizing the chemical and physical properties of secondary aluminas will make them ever more attractive economically also.

Furthermore, the cost of producing those 2,6 Mt of bauxite/alumina by conventional means is orders of magnitude greater than the production cost of secondary alternatives such as Valoxy®.

5 RVA recycling process

The RVA process comprises four main stages (Fig. 5).

Firstly, salt slag is milled with optional recirculation to liberate aluminium by eddy current separator and iron by magnet (Fig. 6).

As in many aspects of production, milling demands a compromise between two conflicting parameters: if the slag is milled too fine, valuable aluminium particles are lost as dust; conversely if the milling is too coarse more slag is left adhering to the granule. This ultimately means less efficient dissol-

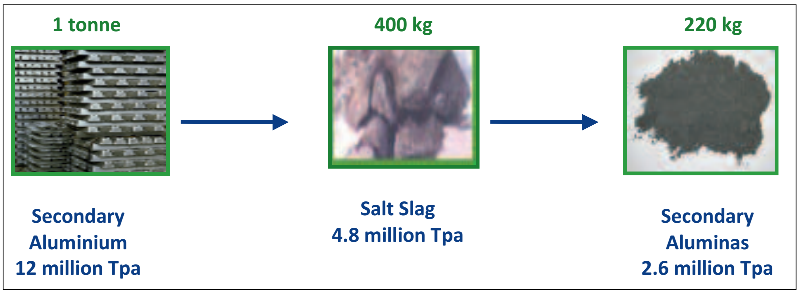

Fig. 4 Estimated global potential of secondary aluminas

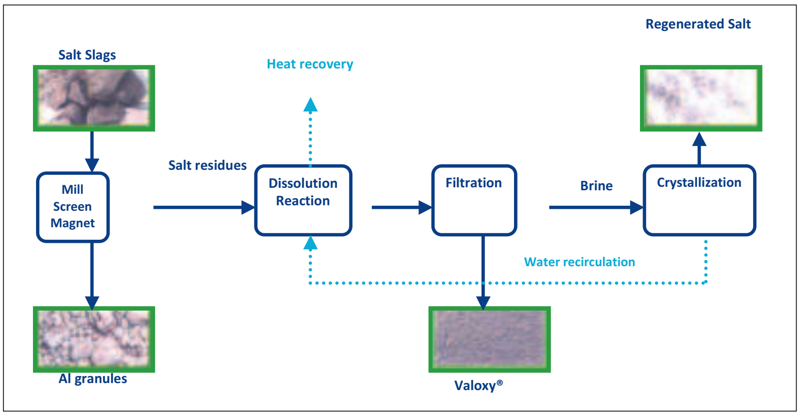

Fig. 5 RVA process flow chart showing three main outputs: aluminium granules, salt and Valoxy

Fig. 6 Mill plant

Fig. 7 De-duster serving the mill plant

ution/reaction and more free aluminium in the Valoxy® – the latter limiting Valoxy®'s application options. Fine particulate from the mill plant is removed by the de-duster (Fig. 7).

Next, the remaining salty material is introduced to a dissolution section where it is mixed with water (recovered later in the process). The ensuing slurry is pumped into pressurized reaction vessels where it is agitated as the reaction temperature rises. Gaseous reactants are produced including hydrogen, methane and ammonia. These are incinerated and exhausted from the stack. Energy from the waste gases is recovered for other parts of the process. RVA recently commissioned an additional reactor vessel (Fig. 8).

The new reactor greatly upgrades the destruction of precursors to noxious gases within the slag. This is particularly important with respect to ammonia emissions: hydrolysis of residual nitrides in the slag can cause the formation of ammonia on contact with moisture.

The residual from the reaction phase is conveyed to a belt filter (Fig. 9). Brine and water are sucked out under vacuum, leaving the solid residue, Valoxy®. Clean water and the water removed in the dissolution stage are used to washed the solids.

Finally, the effluent brine continues to the three stage crystallization section. Three vessels operate in series stepping down temperature and pressure in succession. This enables NaCl and KCl to be crystallized out of solution, initially separately and then in combination, under optimal conditions to bring the salt mixture to the required specification. An in-line decanter (Fig. 10) increases the concentration of solids in the slurry and facilitating higher salt recovery. The final mixture salt is conveyed to storage bays for onward shipment back to the secondary aluminium refiners. Water recovered from the crystallizers is recirculated back to the dissolution section.

A proprietary computerized control system monitors the whole process to ensure that key variables remain within pre-defined limits and outputs meet stringent specifications. RVA's slag recycling process is a closed-loop system making minimal demands on the environment: there is no solid waste; water used for washing is recirculated; gaseous emissions are incinerated to harmless residues and ammonia gas is neutralized by dedicated scrubbers (Fig. 11).

Fig. 8 New reactor

6 Valoxy® – a secondary alumina

From a minerals point of view, the most interesting of the three outputs at RVA is Valoxy®, an effective low cost source of alumina for non-metallurgical applications.

Fig. 9 Filter plant

Fig. 10 Brine decanter

Fig. 11 **Gas scrubber**

Chemically, the alumina content of Valoxy® is typically around 70 %. The balance is silica, magnesia and other oxides (Tab. 1).
A typical mineralogical analysis of Valoxy® (Tab. 2) shows that alumina is present in several forms including $Al(OH)_3$ [gibbsite], AlO(OH) [boehmite] and $MgAl_2O_4$ [spinel].
Particle size distribution of Valoxy® indicates that most grains fall within the silty region namely, 2,5–62,5 µm (Tab. 3).

Tab. 1 **Valoxy® – typical chemical analysis (dry weight)**

Component	Typical content [%]
Al_2O_3	70
MgO	10
SiO_2	6-8
CaO	2
Na_2O/K_2O	2,3
F^-	0,4
Cl^-	0,5

Tab. 2 **Valoxy® – typical mineralogical analysis**

Phase	Formula	Average [%]
Spinel	$MgAl_2O_4$	33,0
Boehmite	AlOOH	24,7
Corundum	Al_2O_3	14,9
Glass	$AlMg_3Na_4Si_{38}O_{50}$	8,1
Nordstrandite	$Al(OH)_3$	4,7
Bayerite	$Al(OH)_3$	4,6
Quartz	SiO_2	1,5
Fluorite	CaF_2	1,4
Goethite	FeOOH	1,1
Diaspore	AlOOH	1,0
Periclase	MgO	1,0
Halite	NaCl	0,8
Aluminium	Al	0,8
Calcite	$CaCO_3$	0,7
Gypsum	$CaSO_4$	0,7
Magnetite	Fe_3O_4	0,5
Silicon	Si metal	0,3

Tab. 3 **Valoxy® – typical particle size distribution**

Fraction [%]	Average [%]
>500 µm	11,6
100–500 µm	28,1
40–100 µm	12,4
<40 µm	47,9
Total	100,0

Tab. 4 Insulating firebricks containing 30 % Valoxy® – selected properties

Service temperature	1400–1450 °C
Density	0,8–0,9 g/cm³
Alumina content	38–42 %
Compressive strength	2,8–4,7 MPa

7 Valoxy® – Application in thermal insulation

As well as low price and stable supply, Valoxy® offers producers the potential for technical benefits based on its nominal alumina content of around 70 %. Valoxy® was evaluated as the alumina source for insulating firebricks. Insulating firebricks containing 30 % Valoxy® bricks were successfully used to insulate the roof of kiln cars. The bricks exhibited properties similar to the standard, ASTM 26 (Tab. 4).
Standard fireclay mixes containing Valoxy® were tested for two parameters commonly used to evaluate ceramic applications:
- volume shrinkage
- fired water absorption.

Per cent volume shrinkage measures the extent to which a clay body shrinks when it is fired. The lower the shrinkage the more robust the ceramic structure at the given firing temperature. In trials, a typical fireclay fired at 1250 °C shrank by around 15 %. By contrast, as Valoxy® was increasingly substituted for fireclay (up to 40 %) in the mix the volume shrinkage was reduced. This suggested Valoxy® was having a positive influence on the ceramic lattice (Fig. 12).
Fired water absorption measures the open pores and channels within the interior micro-structure of a fired clay body. The more open or porous the ceramic lattice the more resistant it is to firing shrinkage. The progressive substitution of Valoxy® up to 50 % in standard fireclay fired at 1250 °C resulted in increases in fired water absorption (Fig. 13). By implication, Valoxy® was having a positive influence on the ceramic structure making it more open, more stable and more resistant to shrinkage.

8 Valoxy® – sound economics and good for the environment

Why does a secondary alumina material such as Valoxy® make commercial sense for the producer of thermal insulation materials? Most industrial businesses try to avoid shocks. Valoxy® derives from an established industrial process. It is not subject to the vagaries of extraction from natural sources and the variability associated with a global commodity. As a result supply is predictable. Though influenced by the supply/demand balance for bauxite and alumina, pricing for secondary alumina is driven predominantly by the economics of salt slag processing.


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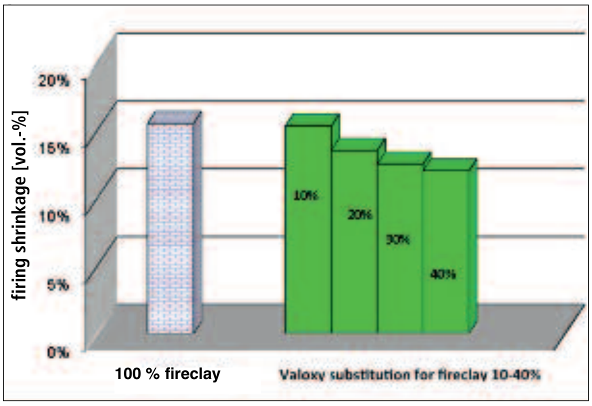

Fig. 12 Volume firing shrinkage at 1250 °C resulting from partial substitution of fireclay by Valoxy®

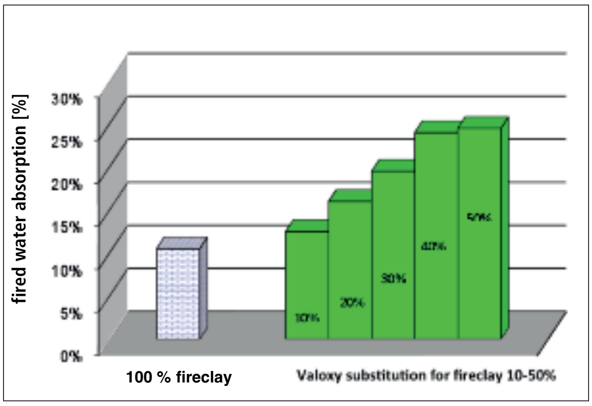

Fig. 13 Fired water absorption at 1250 °C resulting from partial substitution of fireclay by Valoxy®

This enables long-term pricing structures at levels which are very attractive compared to bauxite and alumina. Based on the chemistry and initial applications data, there is the potential for downstream savings in operating cost. These of course need to be confirmed in process-specific evaluation by potential users. Weight for weight, the alumina content of Valoxy® costs a fraction of alumina from conventional sources.

Finally, from an environmental point of view, Valoxy® is a sustainable material: every tonne of bauxite substituted by Valoxy® is a tonne less that has to be dug out of the ground. Valoxy is classified by the French environmental authorities as non-hazardous. The material may therefore be freely traded across the EU and beyond.