A synthetic source of alumina from aluminium slags

RVA takes slags from aluminium smelters and recycles them into three value-added outputs, including an unconventional source of alumina for non-metallurgical applications

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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 secondary material streams, one metallic and two mineral–based. Being derived from an established recycling process, RVA's secondary materials offer supply and price stability - a sharp contrast to the vagaries of virgin material extracted from nature.

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."

[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.

The molten salt layer performs two main functions:

1. Salt coats the metallic aluminium in the melt phase hence minimizing oxidation losses.
2. 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 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.

From waste to valuable raw materials

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

- 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.
- Aluminium oxide-based material with the trade name, VALOXY®. Valoxy comprises around 70% alumina by weight and is offered as a substitute for bauxite/alumina in non-metallurgical (non-Bayer) applications.

All three streams are therefore returned to productive use in a double loop recycling process (Figure 1). Commercial arrangements for salt and granules vary from customer to customer. In some cases, slag is toll-converted at a contracted fee per tonne slag received. The resulting granules and salt are delivered back to the slag supplier as part of the agreement. In other cases, the toll conversion agreement covers the return of salt but not granules. Valoxy, by virtue of its special chemistry, is subject to entirely separate commercial procedures, unconnected with the refiners who supplied the slag.

RVA's aluminium granules are available in three size bands (Table 1).

Particle size	Indicative Al yield on melting
0.5 - 2 mm	≥ 60%
2 -10 mm	≥ 80%
>10 mm	≥ 80%

Table 1. Indicative aluminium yield per grain size

The salt mixture is geared to the needs of aluminium refiners. It thus has the following chemical and physical properties (Table 2):

Parameter		
NaCl	67% w/w	
KCl	30% w/w	
CaF_2	2% w/w	
Moisture content	<3%	
Melting point	670°C	
pH in solution	Neutral	
Granulometry	0 - 200 µm	50%
	200 - 600 µm	50%
Bulk density	1.4 kg/L	

Table 2. RVA reconstituted salt mixture – key chemical and physical properties

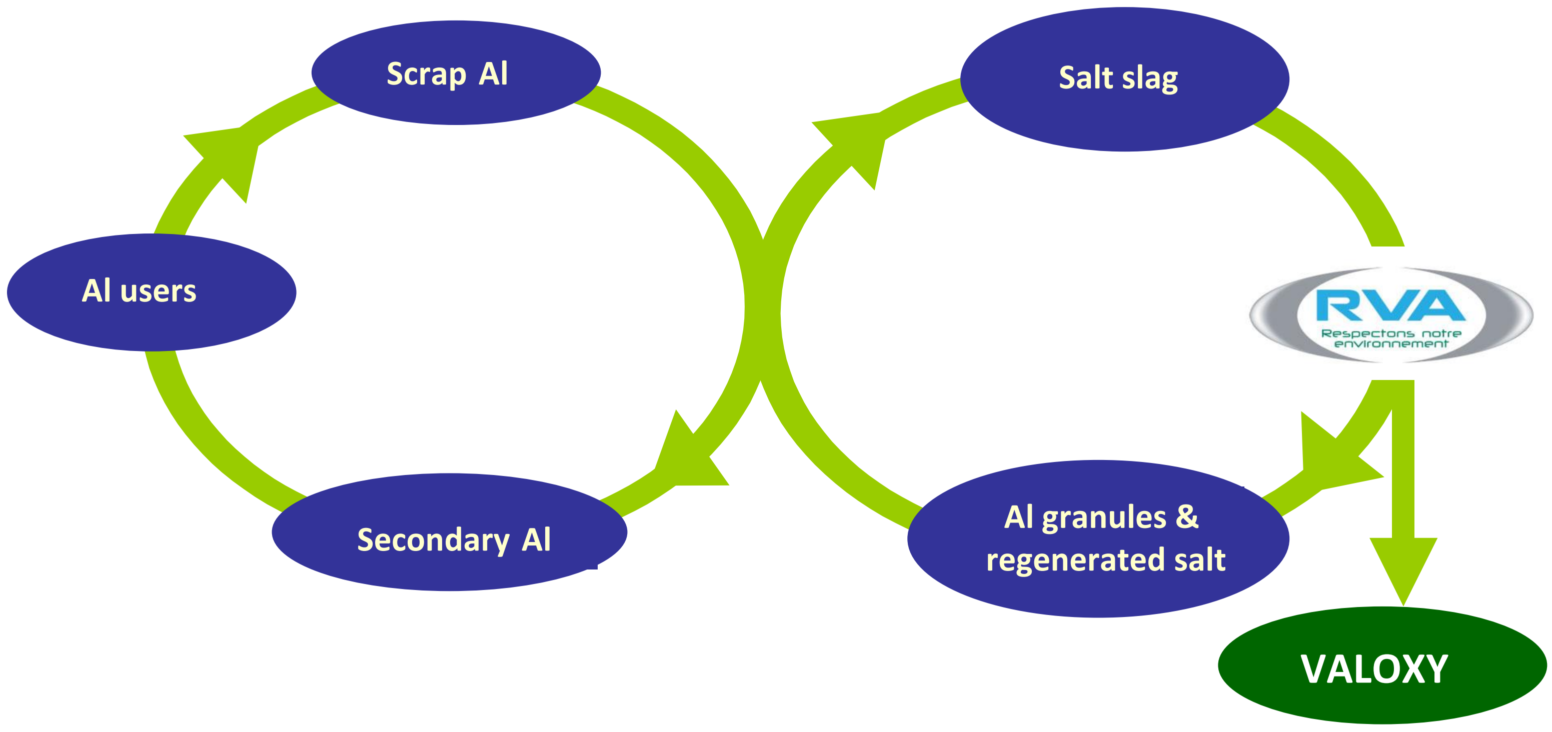

Figure 1. Material flows from salt slag to value-added raw materials

The market for salt slag treatment

Since secondary aluminium production is largely dependent on molten salt, global 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 2009 worldwide secondary aluminium production stood at around 11 million tonnes. Taking a conservative figure of 400 kg slag/tonne aluminium, salt slag arisings may be estimated at 4.4 million tonnes worldwide (Figure 2). The distribution of salt slags around the world follows the distribution of secondary aluminium production. This means around 900,000 tonnes of slag are generated annually in Europe, 1.2 million tonnes in the US and China, now the dominant player, currently generating around 1.6 million tonnes of salt slag p.a.

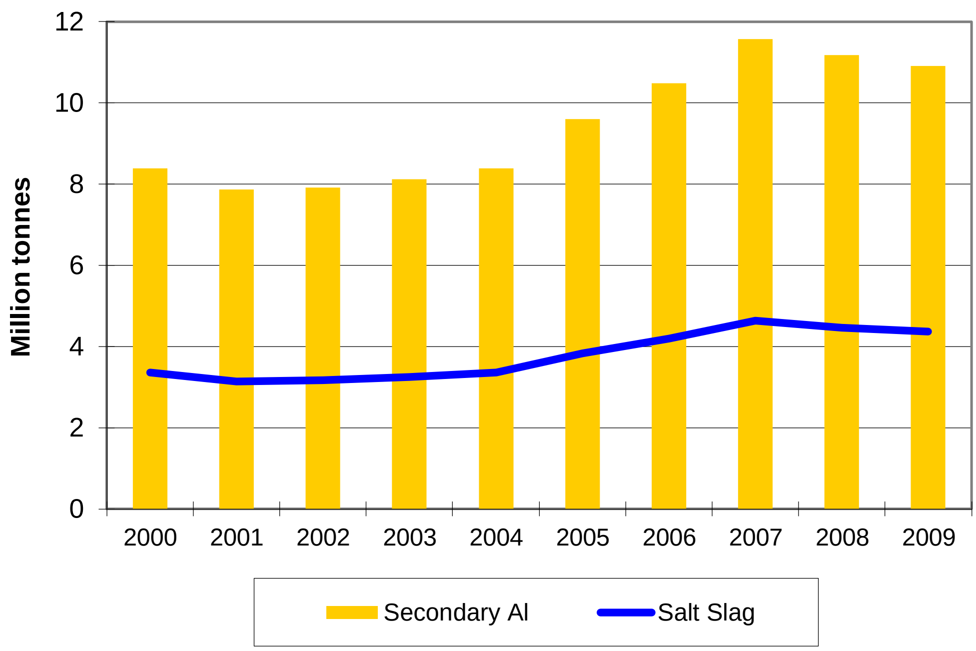

Figure 2. World arisings of salt slag - a function of secondary aluminium production

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 alumina-rich material, VALOXY, is derived (Figure 3).

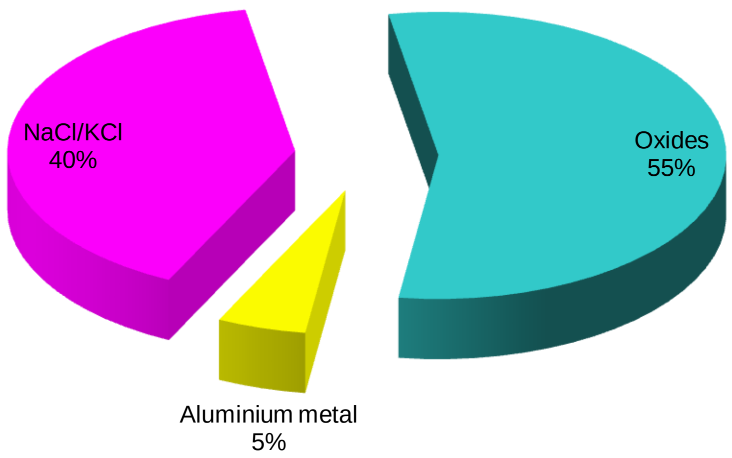

Figure 3. Typical composition of salt slag

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 Valoxy-type alumina. The global potential output of such alternative aluminas can therefore be estimated at around 2.4 million tonnes per annum (Figure 4). However, this material is not immediately available worldwide. The production of alternative 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 much 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 source of bauxite/alumina-type material. Utilizing the chemical and physical properties of these alternative sources of alumina will make them ever more attractive economically also.

Furthermore, the cost of producing those 2.4 million tonnes of bauxite/alumina by conventional means is orders of magnitude greater than the production cost of alternatives such as Valoxy.

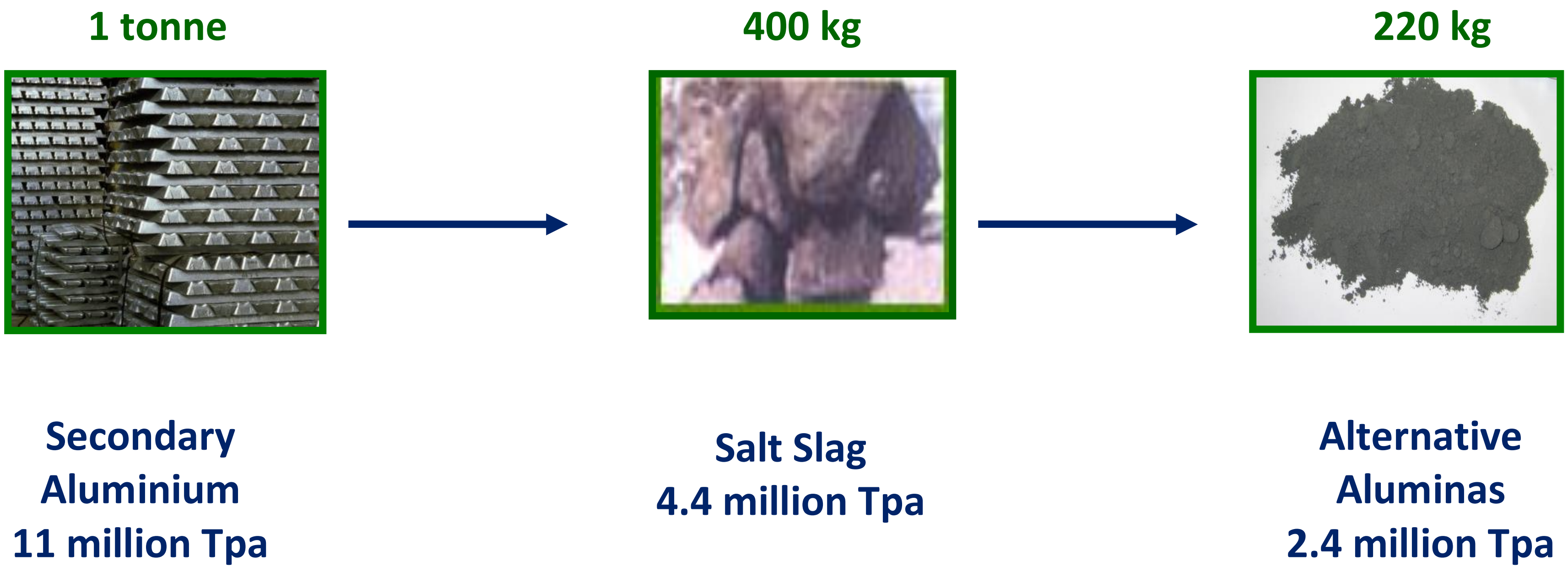

Figure 4. Estimated global potential of alternative aluminas

RVA recycling process

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

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

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 dissolution/reaction (see next stage below) 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.

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.

The new reactor will greatly upgrade 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. Previously, such nitrides were present in small quantities in the Valoxy giving the material an ammonia smell. Initial indications are that the new reactor, will reduce the odour.

The residual from the reaction phase is conveyed to a belt filter.

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 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 is neutralized by dedicated scrubbers.

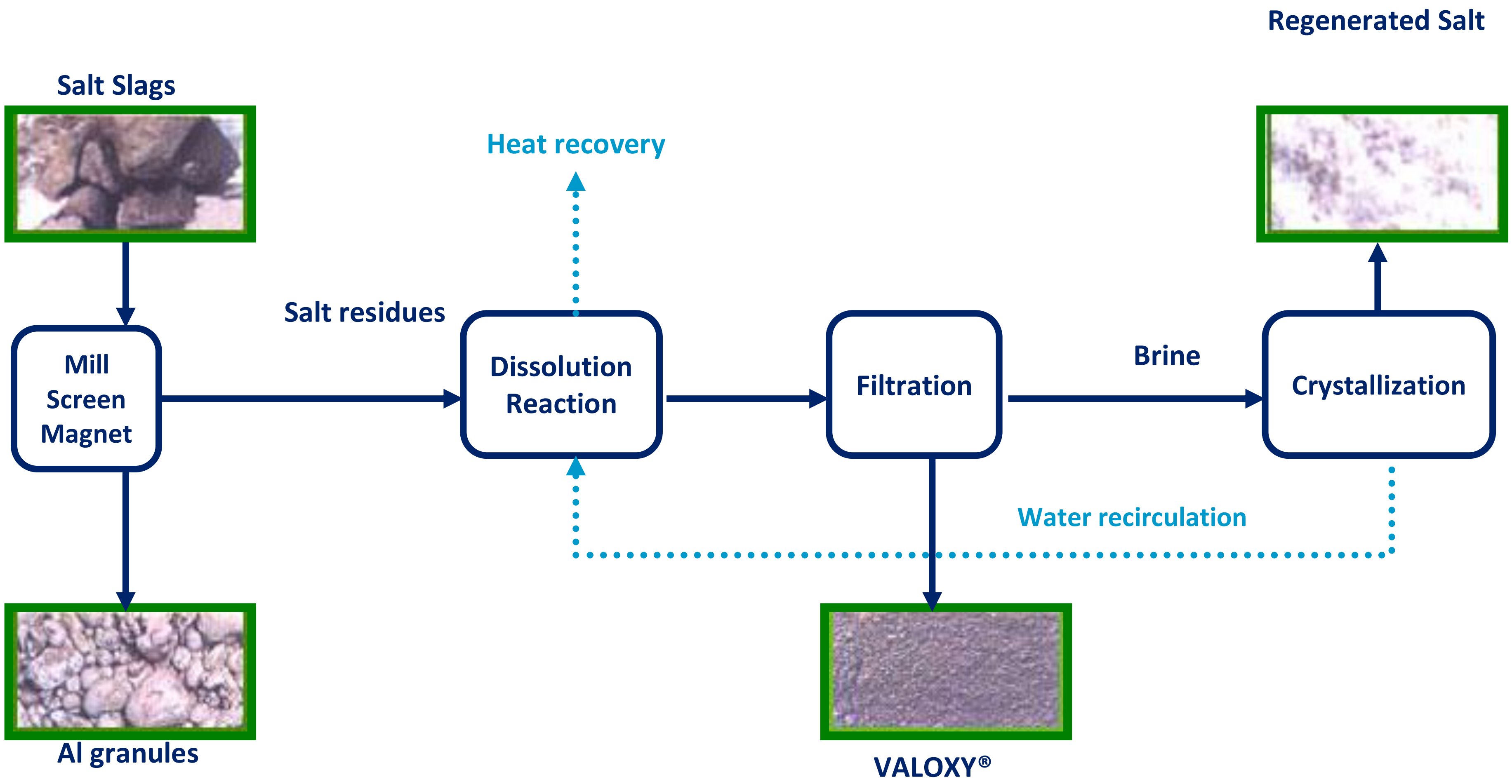

Figure 5. RVA process flow chart showing three main outputs: aluminium granules, salt and VALOXY

For a minerals point of view, the most interesting of the three outputs at RVA is Valoxy. RVA offers Valoxy as an alternative to alumina/bauxite in non-Bayer applications such as cements, binders, bricks, aluminates and refractories.

Alumina content of Valoxy is typically around 70%. The balance is silica, magnesia and other oxides (Table 3).

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%

Table 3. VALOXY - Typical chemical analysis (dry weight)

Particle size distribution of Valoxy indicates that most grains fall within the silty region namely, 2.5-62.5µm (Table 4).

Particle Size Banding	%
<2.5 µm	12.7
2.5 - 62.5 µm	68.7
62.5 - 250 µm	17.6
250 - 500 µm	1.0

Table 4. VALOXY - Typical particle size distribution

As well as low price and stable supply, Valoxy potentially offers technical benefits also. Processes using non-metallurgical alumina are many and varied making it difficult to generalize. Nevertheless, different properties of Valoxy could contribute energy savings and/or easier processing of the raw material mix. As such, Valoxy could wholly or partially replace bauxite in many applications including:

- *Cement clinker*
  Valoxy has proven to be a valuable additive in cement manufacture. Valoxy may be used to introduce alumina into the clinker burning process of the cement kiln. High alumina content is important for the formation of calcium aluminate

complexes in the cement. Moreover, Valoxy's fluorspar content enables the formation of a calcium fluoride/calcium aluminate-based mineral important to cement production.

- *Refractories and ceramics*
  Materials resistant to high temperature are made from materials such as alumina, bauxite, corundum, spinelle and aluminate cement. Valoxy may act as a source of alumina in ceramic and refractory applications. In addition, independent studies have demonstrated that Valoxy may replace fireclays in the production of clay products.
- *Chamottes*
  The most common source of material for fireclay refractories are fireclays – naturally abundant sedimentary rocks. The performance of low-grade refractories may be enhanced by the addition of alumina-based chamottes. Compared to traditional chamottes such as quartz sand, Valoxy demonstrates performance and cost advantages. In certain applications, Valoxy maintains a thermally stable and open structure on firing and avoids the problem of micro-cracking associated with quartz inversion on cooling.
- *Mineral wool*
  Alumina is added in the manufacture of mineral wool to reduce solubility of dust particles in lung fluids preventing bronchial problems for operatives. Valoxy may have a role as the alumina source.
- *Stainless steel slag conditioning*
  A recent lab-scale study demonstrated that Valoxy improved the properties of AOD slag from stainless steel production, compared to traditional treatments such as boron. Treatment with Valoxy resulted in a slag with similar micro-hardness, improved chromium entrapment and better microstructure (lower porosity) compared to boron. This offers stainless steel producers the potential for significant economic benefits due to:
  (a) Valoxy’s low cost compared to born
  (b) The higher value the slag could achieve as a construction aggregate.
- *Geopolymers*
  Valoxy may have a role as the aluminosilicate source in the basic geopolymerization reaction. Combined with a highly alkaline solution, Valoxy may be a precursor for geopolymeric materials offering improved heat resistance produced at a much lower temperature than traditional fired products.

For the above applications, even partial substitution of bauxite/alumina by Valoxy could substantially reduce formulation raw material costs.

Valoxy is classified by the French environmental authorities as non-hazardous. The material may therefore be freely traded across the EU and beyond.

Valoxy is constantly being tested in a wide variety of applications by leading manufactures for whom alumina/bauxite is a vital raw material. The range of opportunities for incorporating Valoxy in traditional alumina applications is wide indeed. Secondary materials such as Valoxy are fascinating. However, it often takes the synergy with complementary expertise to really bring out the full economic potential. That is why, in addition to direct off-the-shelf use, RVA is working with partners in different application sectors to see how Valoxy can be best utilized in their production process.

Such collaboration may be:
• Fundamental development through re-engineering the chemistry of the material
• Research into new or existing applications
• Or taking Valoxy into new markets, geographically or functionally.

Why does a secondary alumina material such as Valoxy make commercial sense for the user? 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 will be driven predominantly by the economics of salt slag processing. 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. 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.

About RVA

RVA's origins go back to 1989 when the company began with a simple dross milling operation. Today RVA treats around 80,000 tonnes of salt slag per annum. It is the only slag treatment plant in France and one of only two salt slag re-processors in western Europe. The company is located in the picturesque village of Les Islettes, 200 km east of Paris and only 100 km from the German border. RVA is therefore well placed to service and supply customers across western Europe.

The slag processing sector consolidated considerably in 2009 when Befesa (Spain), acquired Aluminium-Salzschlacke Aufbereitungs GmbH and Alsa Süd GmbH, wholly-owned subsidiaries Agor AG . The provision of salt slag treatment is likely to remain concentrated in western Europe and new processors are not currently expected to emerge. The economics of slag recycling are largely driven by transportation costs. Markets are therefore fairly regionalized with minimal competition between industry players.

By providing a critical environmental service and supplying useful secondary products, RVA is playing its part in securing Europe's raw material supply line. That should mean smiles all round in Brussels. What is more, bauxite supply solutions may come full circle from discovery of natural bauxite in one French village (Les Baux-de-Provence in 1821) to production of synthetic bauxite in another (Les Islettes in 2011).

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