

News from ALSA's secondary alumina

1. Summary

As already published at the Athens Bauxite seminar in 2007 (7), the salt slag processor ALSA continues offering high alumina products under the brand SEROX from their ecologically sustainable production facilities.

SEROX is a non-conventional alumina product for a couple of proven and potential uses such as mineral wool, cement clinker, secondary steel slag, construction materials etc.

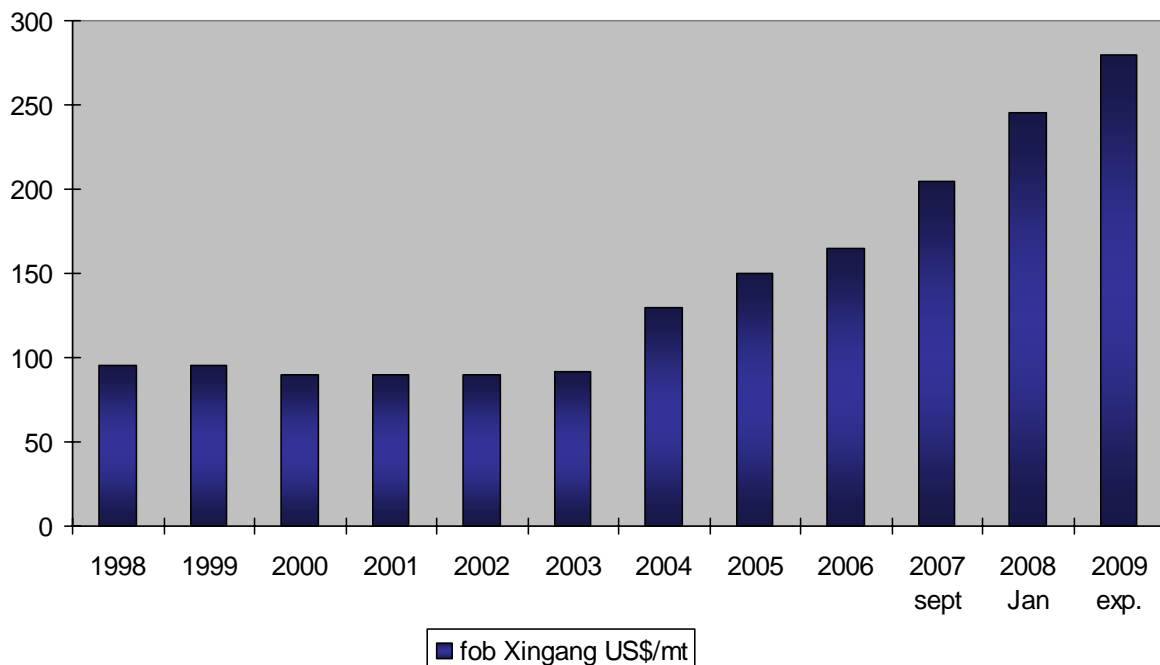
Facing rampant bauxite prices and an increasingly tight alumina market, ALSA offer different grades of SEROX based on a growing production capacity.

Thus, ALSA is generating a safe source of high quality raw materials as a new alumina commodity of reliable local availability and attractive price structure.

ALSA is now as before highly committed into a process of upgrading their products and developing new utilization lines.

2. Secondary Alumina made by ALSA

picture 1: rampant price of rotary kiln grade bauxite from China



Looking down upon picture 1 some alumina purchasing departments may be supposed to think about alternative ways of getting supplied their Alumina need.

And in fact, there are some ideas about such alternative ways.

For example, Alumina can be reclaimed when processing Aluminum salt slags.

Aluminum salt slags respectively salt cakes occur when melting both scrap aluminum and aluminum dross for recovering and recycling aluminum metal back in the product life cycle.

Depending on the employed smelting process, these aluminum salt slags consist of between 20% and 60% melting salt, up to 10% aluminium metal and above all various oxides (35% to 75%).

The “oxides” is a mixture predominantly of aluminium oxide (corundum), aluminium hydroxide, Mg-spinel and silica. Its composition can fluctuate considerably depending above all on the metal alloys being melted.

Table 1 show the range of chemical composition of the oxides from the Aluminum salt slags respectively cakes.

Table 1: range of chemical composition of oxides

<u>Compound</u>	<u>% by mass, (dry substance)</u>
Al ₂ O ₃	60 ... 80
MgO	1 ... 10
SiO ₂	1 ... 12
CaO	1 ... 5
Na ₂ O+K ₂ O	1 ... 7
N	0.5... 10
F	0.5... 11
Cu	0.1... 0.5

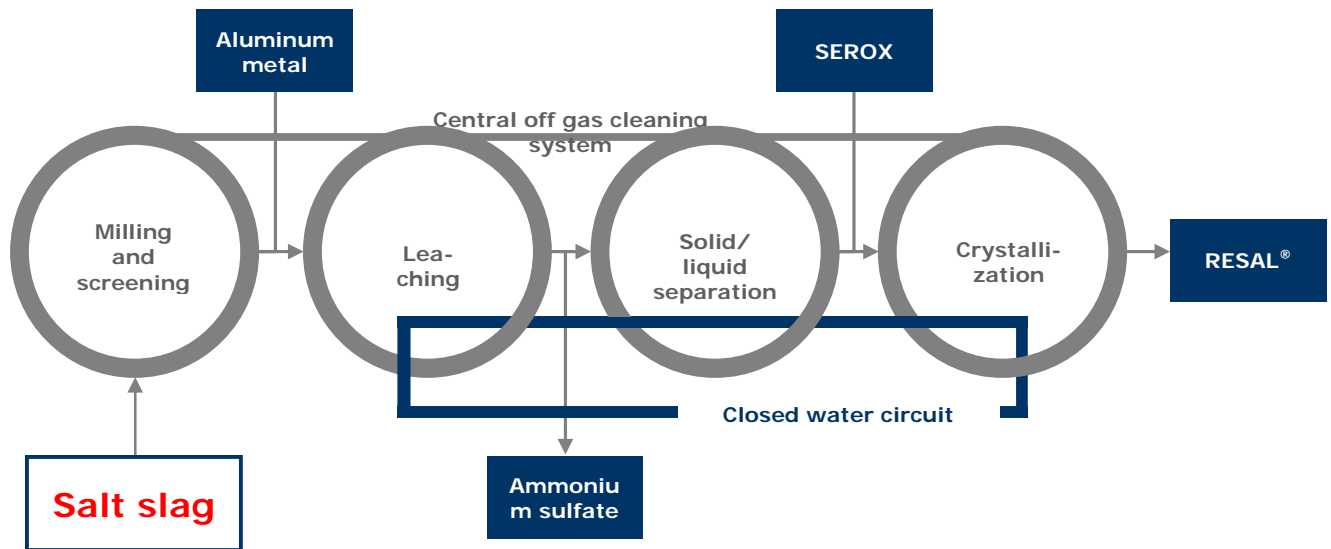
Especially the oxides deriving from the primary aluminum dross smelting may contain considerable amounts of Alkalies and Fluorides those can spoil some use.

ALSA (at present a subsidiary of AGOR AG) was the first company to employ techniques in their plants for recovering each and every of the valuable components from aluminum salt slags.

Since the middle of the 1980's, ALSA have shown that all the products (Al-granulate, melting salt and oxides) can be produced in stable quality, and can also be reintroduced into the market place.

The picture 2 shows a simplified flow sheet of ALSA's salt slag processing technique.

Picture 2: simplified flow sheet of the ALSA processing technique



The aluminum metal granulates and melting salts (RESAL) have in the meantime become sought-after raw materials for secondary smelters. The oxides are sold under the brand “SEROX”, as a raw material for the production of cement clinker and rock wool, among others. The process operates without waste, i.e. without land filling.

SEROX is a high-grade Alumina-bearing raw material containing about 66 % of Al₂O₃ (dry condition). The following tables show the chemical and mineralogical characteristics of SEROX from ALSA Germany in comparison to Bauxite.

Table 2: Chemical composition of selected SEROX and bauxite grades according to (1;2;3), (main constituents, % of dry mass):

	SEROX	raw bauxite	Calcined SEROX	calcined bauxite
Al ₂ O ₃	65 - 70	45 – 61	75 – 79	54 - 90
CaO	2 - 4	0.1 – 1.9	2 – 4	0.1 – 0.8
SiO ₂	6 - 12	0 – 15	6 – 13	1 - 40
MgO	4 - 9		5 – 10	0.1 – 0.6
Fe ₂ O ₃	1 - 2	2 – 30	max. 2	1 - 8
TiO ₂	max 0,8	max 6		1.6 - 5
Na ₂ O+K ₂ O	1 - 2		max. 2	0.2 – 1.1
F+Cl	1 – 2		max. 0.1	
Loss of Ignition	6 - 12	13 – 30	max. 0.2	max 0.2

Table 3: Mineralogical composition of SEROX (main constituents, min-max.):

Al-hydroxide [Al(OH) ₃]	30 - 35 %
Corundum [Al ₂ O ₃]	25 - 30 %
Spinel [MgAl ₂ O ₄]	20 - 25 %
Silicates [SiO ₂]	5 - 10 %
Fluorspar [CaF ₂]	1 - 2 %
Aluminium metal [Al]	2 - 3 %

SEROX as supplied by the three ALSA works in Germany is available as three grades:

- SEROX moist: bulk material with a moisture content of about 25 %
- SEROX-T: pump-able and free-flowing silo ware of ard. 3 % moisture
- FE-SEROX: flow-able mixture of SEROX and iron oxide tailored to the customers demand (ard. 20 % moisture)

SEROX can be shipped to the users as follows:

- SEROX-T: by silo trucks, railcars or in big bags
- SEROX moist: as a bulk load or in big bags by truck, rail car and ship
- FE-SEROX: as a bulk load by truck or rail car.

Due to these characteristics, SEROX offers many benefits since it features a constant quality and, even more importantly, is permanently available. Contrary to raw materials sourced from international markets, it offers reliable local availability and thus a safe source of Alumina of an attractive price structure.

Thereby, SEROX has a great potential to replace conventional Alumina bearing raw materials such as bauxites. As a high alumina product, SEROX is suited to introduce Alumina (Al₂O₃) into a couple of lines like cement clinker, mineral wool, synthetic steel slags etc.

In principle even pure Aluminum hydroxide for the production of Aluminum metal could be re-produced from SEROX.

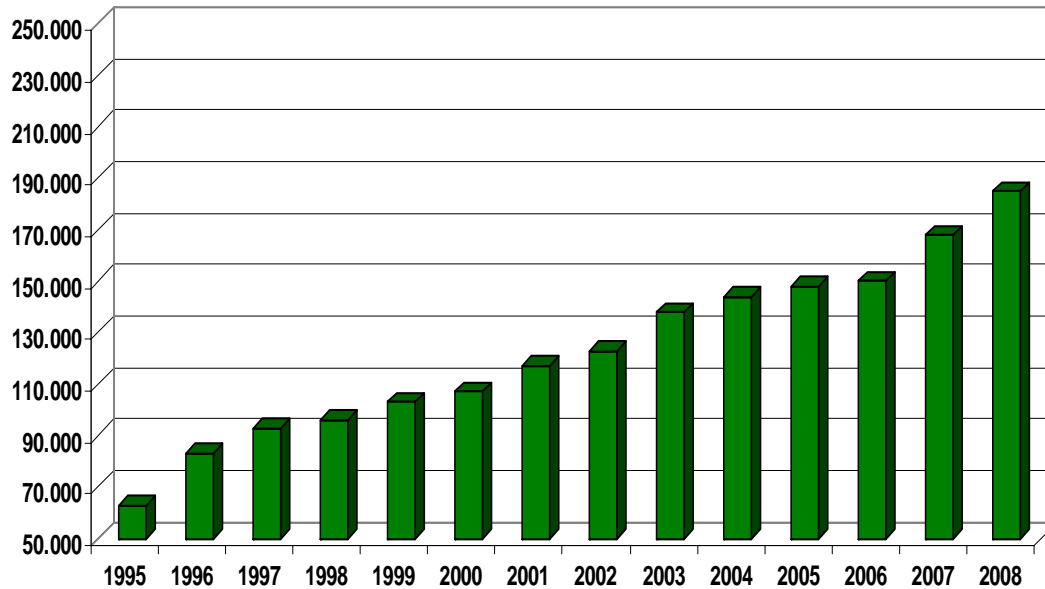
SEROX can be mixed with other fine grained raw materials and / or binders to form pellets or bricks. Lumpy SEROX can also be made by means of Briquetting machines.

ALSA's present SEROX production capacity is distributed as follows (All figures on dry basis and metric tons per year).

- ALSA Hannover/Germany:	65,000	(143,000,000 lb)
- ALSA Luenen/Germany:	105,000	(231,000,000 lb)
- ALSA Süd Toeing/Germany:	50,000	(110,000,000 lb)
- ALSA Canada Becancour/Quebec:	25,000	(55,000,000 lb)

Picture 3 shows the development of ALSA's SEROX production per year.

Picture 3: development of ALSA's SEROX production (mt per year, dry)



In terms of a mass balance, the SEROX production ranges between 50 and 70 percent of ALSA's processing facilities total output.

In the following, the main fields of application and market potentials of SEROX are indented to be shown in a short.

2.1. Portland cement clinker

The first step on ALSA's way towards the complete marketing of SEROX was to develop an alumina additive for the cement clinker production.

Based on acceptable handling properties as well as a stable quality, ALSA was able to introduce their SEROX output into the cement clinker line as early as 1994.

Thereby, it turned out that SEROX can be used not only as a simple Alumina raw material like bauxite, clay etc. to introduce Al_2O_3 into the clinker burning process of a cement kiln. There are a couple of additional advantages deriving from SEROX.

Every Portland cement clinker contains minerals like Tricalciumsilicate (C3S), Dicalciumsilicate (C2S), Tricalciumaluminate (C3A) and Calciumaluminateferrite (C4AF) those are creating the performance and strength of the cement. Alumina is needed to form C4AF and C3A when burning the clinker.

Due to its slight content of fluorspar SEROX does not only help forming these minerals. It forms as well the favourable compound $11CaO \cdot 7Al_2O_3 \cdot CaF_2$. But, the most important job of SEROX is to boost the formation of the main strength creator C3S.

Thereby, SEROX tends to raise the modulus of lime while lowering the modulus of silicate. As a result, the use of SEROX improves the sintering process as well as the early setting strength of the cement.

Caused by a raise of the lime modulus, a clinker of a higher performance will be produced, able to contain more aggregates like fly ash, limestone etc. when being milled down to cement meal. That is the point where the cost cutting kicks in.

Furthermore, by a specifically lower proportion of clinker to produce the same amount of meal, simultaneously the CO₂-emission per ton of cement meal will be decreased. That is a way to save CO₂-certificates.

Usually, depending on the raw materials situation on site, the amount of SEROX added to cement kilns feed ranges from 1 up to 3 mass percent of the total input.

Up to now, ALSA have been supplying successfully a couple of cement kilns in Europe and North America with nearly 2,000,000 metric tons (ard. 4.4 billion lb) of SEROX without any ecologically harmful impact on the environment.

2.2. Mineral wool

In 1997, the European Commission classified certain mineral wools containing more than 18% of an alkali and earth alkali oxides to be potentially carcinogenic substances by the directive 97/69/EC. As already reported earlier in **IM** (2), which was to say, the mineral wools producing process had to be supplied with an appropriate level of additional Alumina.

As early as that time, ALSA was successful in introducing SEROX as a substitute of bauxite into the rockwool production in Germany.

The following table shows the range of chemical compositions of mineral wool fibres (5):

Table 4: Chemical composition of alumina containing mineral wool fibres, (mass %)

SiO ₂	38 – 46
CaO	15 – 38
Al ₂ O ₃	10 – 32
MgO	2 – 10
FeO	0.3 – 7
Na ₂ O	0.3 – 3
K ₂ O	0.3 – 1.3

Non-carcinogenic rock wool fibres those are meeting the aforementioned EU directives specification usually range between 18 and 25 % Al₂O₃ content.

SEROX has proven to be a very suitable raw material for supplying the additionally demanded Alumina.

Thereby, SEROX has simply to be added in a proper way to the common raw materials input mix of a cupola melting furnace, usually consisting of lumpy rock stones, slags, internal recycling materials etc.

One way that has proven favourable to introduce SEROX into the rockwool-producing furnaces is to simply mix it with the other input material fines and recycled fibre waste and form it to bricks.

Depending on the users demand and the available technical feeding system, ALSA offer moist SEROX as well as dry SEROX-T to produce mineral wool. It has been shown that both grades are well suitable.

Here again, SEROX has proven to help saving energy costs by lowering the fuel consumption of the cupola furnaces due to its special fluxing properties. It seems that it dissolves quicker than bauxite in the cupolas melting bath and liquefies the melt.

ALSA have been supplying successfully a couple of mineral wool works in Europe with more than 300,000 metric tons of SEROX since 1998. The SEROX consumption of the mineral wool line shows a considerably rising tendency in Europe. This development might be transferred over to North America in the future.

2.3. SEROX-T

In principle, the lines of cement clinker and mineral wool have been consuming the complete alumina production of ALSA since 1998.

Thereby, ALSA have proven to be a trustworthy raw materials supplier by a long term co-operation with the mentioned two major SEROX user lines.

But, ALSA have been running a permanent product improvement process parallel.

The next steps on ALSA's schedule were improved handling properties and diversification. That is why ALSA started implementing drying facilities for SEROX in their plants in 2004.

Today, ALSA is operating as many as three rotary drying facilities for SEROX. The bone-dry product of those facilities is sold under the brand SEROX-T.

SEROX-T enables much better handling properties than moist SEROX. Worth mentioning is above all that SEROX-T, contrary to moist SEROX, does not show any ammonia smell. It is a free-flowing and pumpable silo ware.

Picture 4: view of the SEROX drying facility of ALSA Hannover



SEROX-T is chemically identical with moist SEROX (see table 2). The following table shows the grain size distribution of SEROX-T.

Table 5: Grain size distribution of SEROX-T from ALSA Hannover

<u>Grain size (microns)</u>	<u>Mass pct. of screen underflow, typical</u>
20	25
30	45
90	70
250	85
500	95
1000	99

At present, ALSA is developing a couple of additional industrial applications on the basis of SEROX-T. Beside the mineral wool industry, worth mentioning is the steel mills secondary metallurgy.

For example, ALSA is currently supplying SEROX-T from its subsidiaries to blenders in the USA and Europe. There, the SEROX can get mixed, palletized or briquetted to form part of special blendings of quick lime and alumina for steel mills secondary slags. These mixings with SEROX are said to show excellent melting properties.

Furthermore, ALSA have discovered that some interesting surface properties can rise from the contained Aluminiumhydroxid. This compound causes a specific surface up to 95 m²/g (475,000 sq. ft /lb) for instance. Materials of these properties are interesting for the building industry.

It is worth mentioning here, that ALSA gets valuable support by a couple of competent marketing specialists of Cofermin Rohstoffe Essen on their way of marketing SEROX-T.

2.4. FE-SEROX

Since there are a couple of cement kilns using as well alumina as iron oxide additives to their raw material mix, ALSA started supplying tailor-made pre-mixes of Iron oxide and SEROX (so called FE-SEROX) to cement kilns in 2005.

Table 6 shows an example of such a pre-mix.

Table 6: chemical composition of a selected FE-SEROX mix for cement kilns (typical composition, mass %)

Al ₂ O ₃	43
CaO	2,5
SiO ₂	4
MgO	5
Fe ₂ O ₃	38
Na ₂ O + K ₂ O	Max. 1
Loss of ignition	6

2.5. Calcined SEROX (SEROX-K)

When calcining SEROX above 1,000 degree Celsius (1,830 F), volatile components like chlorides, fluorides and crystal water will be leaving the material. Thus, a product of a raised alumina content occurs as shown in table 2.

That line is still under development. But, facing the rampant growth of calcined bauxite prices (picture 1) it can easily happen that the calcining costs will pay back.

It is worth mentioning here, that from SEROX, as well shaped as unshaped non-flammable mineral foam products can be made.

Thereby, according to an ALSA owned patent (6), SEROX must be treated in a flash calciner between 700 and 800 °C (1,290.. 1,470 °F) prior to being mixed with a liquid sodium silicate and other ingredients.

The solid foams made from SEROX are fire resistant up to 1,000 °C. They can easily be shaped by cutting after hardening. Depending on additional mixture ingredients and their

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proportions, the density of the light weight solid foam can be range from 0.4 to 0.8 metric tons per cubic meter (38.. 76 lb/ cu. ft).

ALSA are about to develop a special technique to be able to produce solid foams from SEROX-T without prior calcining.

3. Literature/References:

- (1) E. D. Sehnke: Bauxite - a global review, Ind. Minerals, Aug. 1995, pp. 39-51
- (2) Zhong Xiangchong: Refractory Bauxite- The next generation. Industrial Minerals, Jan. 2006, 54-61
- (3) Tim Geldmacher: Bauxite data sheets of Cofermin Rohstoffe GmbH, 2008
- (4) Mike O'Driscoll: Alumina in a spin: Industrial minerals, aug. 2006, pp: 36-43
- (5) T. Knudsen, M. Guldberg, V.R. Christensen, S.L. Jensen: New type of stonewool (HT fibres) with a high dissolution rate at pH =5. Glastechn. Ber. Glass Sci. Technol. 69 (1996) No. 10, 331-337
- (6) R. Feige, G. Merker: Porosierender, erstarrungsbeschleunigender Bindemittelbaustoff-Zusatz und Verfahren, European patent EP 1 180 504 A1, 2002, (and US 6,593,262 B2 Porosifying, solidification-accelerating additiv for binding agent building materials, an process ...)
- (7) G. Merker: ALSA are developing secondary aluminas, paper of the 13th bauxite seminar, Athens 2007