# ALSA are developing secondary aluminas

## 1. Summary

The trend in the aluminium recycling market is towards total recycling.
In the future it will be a matter of re-circulating the previously landfilled Aluminium salt slags to the production chain and of re-processing it into saleable products.

In the growing field of Aluminium salt slag reclamation there are a couple of competitors available. Out of them, despite of operating technically similar processing facilities, only very few have reached a waste-free operation.

ALSA for example has demonstrated the feasibility of there waste-free treatment processes by its plants at Hanover and Lünen in Germany for more than 20 years.

Under the roof of the AGOR group, ALSA offer high alumina products under the brand SEROX from their ecologically sustainable production facilities.

Despite their proven quality in many fields of application, the shortages of convential alumina, respectively bauxite, are not to be denied. There availability has become an issue. Now there is an alternative: SEROX.

SEROX is a non-conventional alumina product of a great potential of uses such as mineral wool, cement clinker, secondary steel slag etc.

Facing raw material markets featuring generally rising prices and a partly unsupplied need of alumina, ALSA offer different grades of SEROX based on a steadily growing production capacity.

Thus, ALSA offer a safe source of high quality raw materials as a new commodity of reliable local availability and a reasonable price structure.

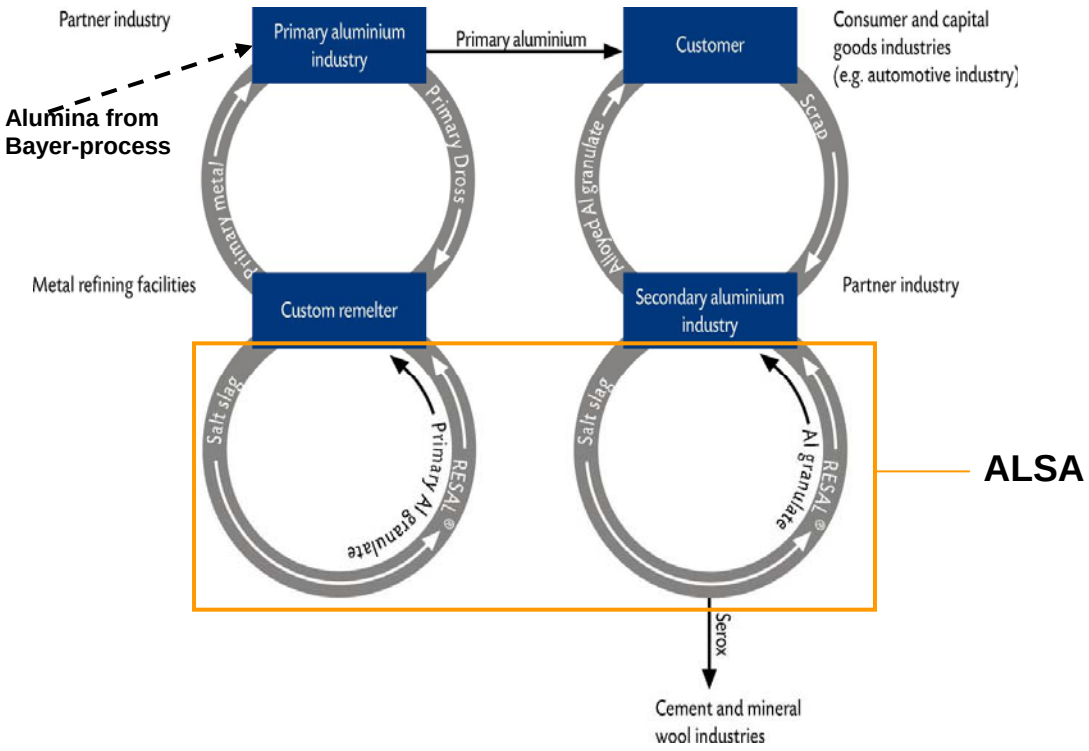
With the help of very able marketing partners - Cofermin Rohstoffe GmbH Essen - ALSA continue to develop various new applications of SEROX. ALSA are happy to be able to utilize the marketing expertise, the exellent industry contacts and the transparent work with this team of professionals.

## 2. About the origin of SEROX

The worlds main source of aluminium metal is bauxite.
There are well known techniques and giant facilities available to produce primary aluminium metal from bauxite by the primary smelters electrolysis based on calcined alumina from the Bayer-process.

On the other hand, Aluminium is a recycling-friendly material.
As a result, in the developed industrial countries, stable closed loop cycles have been developed to ensure repeated use of the metal.

Pict. 1: present life cycles of Aluminium metal




As can be seen in picture 1, primary metal from the primary smelters is cast into various products and after the actual use has been finished, the metal is returned as scrap to the secondary smelters where it is re-melted and returned to the market place.

Dross is produced at various stages in the melting process in the aluminium primary and secondary smelters and foundries. It consists primarily of aluminium metal (40 to 80 %) and oxides of aluminium and its alloy metals.
The aluminium metal included in the dross can be partially recovered by re-melting or by milling and screening.

So called Aluminium salt slags respectively salt cakes occur when melting both scrap aluminium, and dross for recovering and recycling aluminium metal in the product cycle.
This smelting is done by batches for example in rotary furnaces of various designs, with the addition of varying quantities of melting salt which covers the surface of the molten aluminium metal.

The melting salts used are mixtures of KCl and NaCl (55 to 95 % NaCl). Various fluxing agents, such as fluorspar or cryolite, can also be added to the melting salt mixtures to lower its melting point.

At the end of the smelting process the metal and slag are cast separately.

Per metric ton of re-molten Aluminium, between 300 and 800 Kg of salt slags occur.

Depending on the smelting process employed, these aluminium salt slags consist of between 20% and 60% melting salt, up to 10% aluminium metal and above all various oxides (35% to 75%).
Thereby, unlike the specific melting salt content in aluminium salt slags, the oxide content is expected to be permanently growing.

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

Table 1 shows the range of chemical composition of the oxides of the Aluminium salt slags respectively cakes.

**Table 1**: range of chemical composition of oxides

| compound | % by mass, (dry substance) |
|---|---|
| $Al_2O_3$ | 60 … 80 |
| MgO | 1 … 8 |
| $SiO_2$ | 1 … 10 |
| CaO | 1 … 5 |
| $Na_2O+K_2O$ | 1 … 7 |
| N | 0.5… 10 |
| F | 0.5… 11 |
| Cu | 0.1… 0.5 |

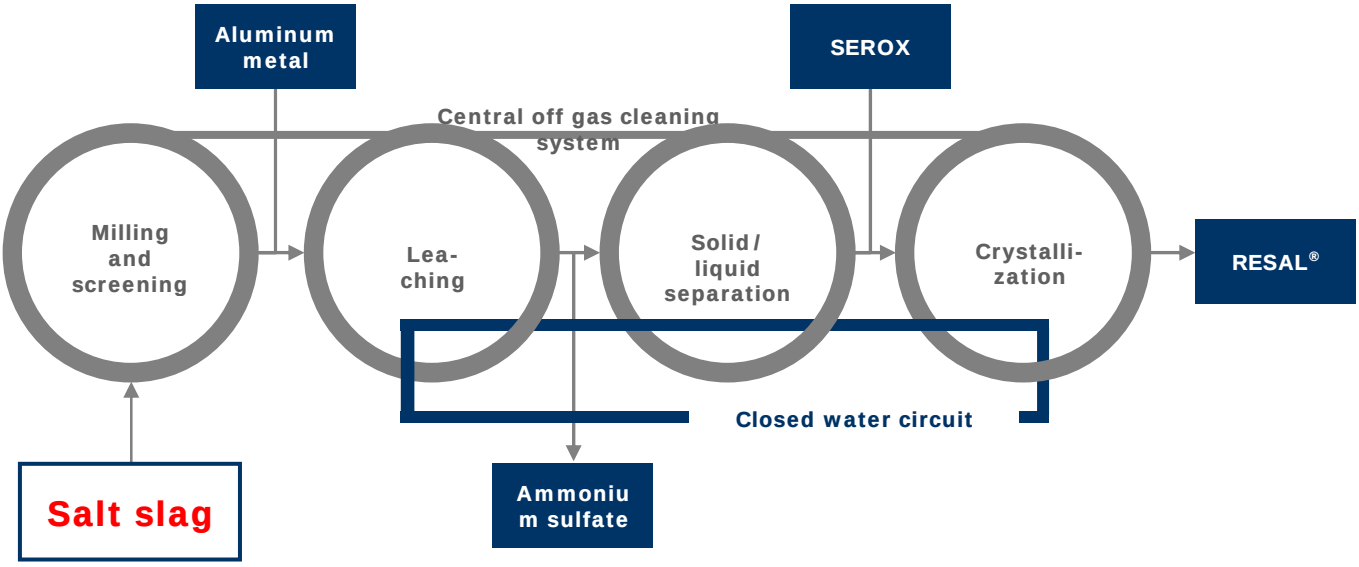
It was until 20 years ago that aluminium salt slags represented the end of the economically useful aluminium metal cycle.
They were (and still are) dumped in landfill sites as waste, although they contain substantial amounts of valuable substances. Salt slag was only processed in a few rare instances; the only recovery practiced was generally the relatively simple recovery of coarse metal particles by dry crushing and screening (i.e. nugget picking).

ALSA (at present a subsidiary of AGOR AG) was the first company to implement processes in their plants for recovering all the valuable components, starting in the middle of the 1980s in Germany.

Since then, ALSA have shown in their plants in Germany that in principle, all kinds of aluminium salt slags can be processed.
They have also 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 flowsheet of ALSA’s salt slag processing technique.

Picture 2: simplified flowsheet of the ALSA processing technique




The metal granulates and melting salts 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 and rock wool, among others. The process operates without waste, i.e. without land filling.

Picture 3: ALSA’s treatment facility at Hannover/ Germany


**3. Quality and quantity of SEROX**

SEROX is a high-grade Alumina-bearing raw material containing about 66 % of $Al_2O_3$ (dry condition). The following tables show the chemical and mineralogical characteristics of SEROX from ALSA Germany.

**Table 2:** Chemical composition of SEROX and metallurgical raw bauxite according to (1), (main constituents, % of dry mass):

| | SEROX | bauxite |
|---|---|---|
| $Al_2O_3$ | 63 - 67 | 50 - 55 |
| CaO | 2 - 4 | 0.1 – 1.9 |
| $SiO_2$ | 7 - 14 | 0 - 15 |
| MgO | 4 - 9 | |
| $Fe_2O_3$ | 1 - 2 | 5 - 30 |
| $TiO_2$ | max 0,8 | max 6 |
| $Na_2O+K_2O$ | 1 - 2 | |
| Loss of Ignition | 6 - 12 | 13 – 30 |

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

| | |
|---|---|
| Al-hydroxide [$Al(OH)_3$] | ⇒ 30 - 35 % |
| Corundum [$Al_2O_3$] | ⇒ 25 - 30 % |
| Spinel [$MgAl_2O_4$] | ⇒ 20 - 25 % |
| Silica [$SiO_2$] | ⇒ 6 - 10 % |
| Fluorspar [$CaF_2$] | ⇒ 1 - 2 % |
| Aluminium metal [Al] | ⇒ 2 – 3 % |

SEROX as supplied by the ALSA works at Hannover, Luenen and Toeging in Germany is available as three grades:
- SEROX moist: flow-able fines and agglomerates with a moisture content of about 25 %
- SEROX-T: pump-able and free-flowing bone dry product (max. 3 % moisture) below 2 mm grain size
- FE-SEROX: flow-able mixture of SEROX and iron oxide tailored to the customers demand

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 at a reasonable 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 ($Al_2O_3$) into a couple of lines like cement clinker, mineral wool, synthetic steel slags etc.

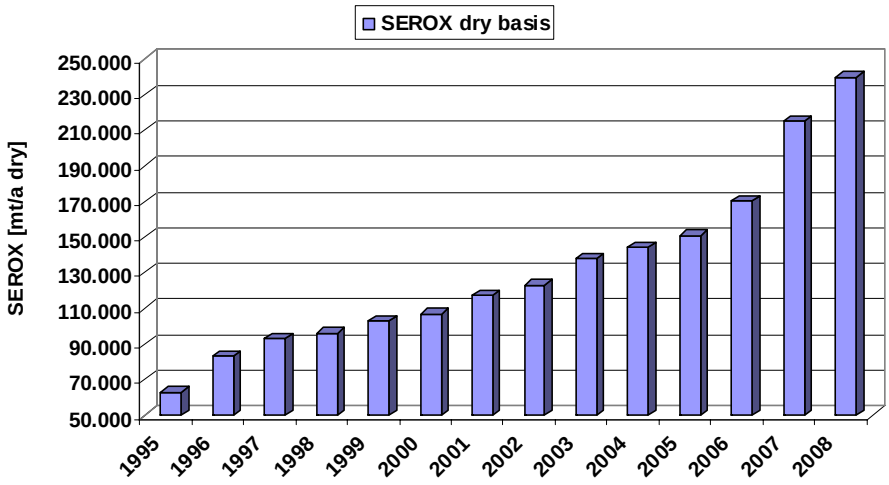
In principle even pure Aluminium hydroxide respectively calcined Alumina for the production of Aluminium metal could be re-produced from SEROX.

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.

SEROX is produced in an industrial scale by ALSA Technologies GmbH – ALSA for short – a member of the AGOR Group, Germany. 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
- ALSA Luenen/Germany : 105,000
- ALSA Toeging/Germany: 50,000 (from April 2007 on)
- ALSA Becancour/Canada: 25,000

Picture 4: development of ALSA's SEROX production




In terms of a mass balance, the SEROX production totals between 50 and 70 percent of the salt slag reclamation plants output.

Since AGOR is pursueing the ambitious aim to expand the treatment capacity of ALSA up to 1 Million mt of salt slag per year until 2010, the yearly output of SEROX is expected to raise to around 500.000 t/ year until that time.

In the following, the stepwise approach of ALSA to the development of a new alumina commodity is intented to be shown.

## 4. first step – SEROX basic applications

### 4.1. Portland cement clinker

Starting some investigation in the middle of the 1980's, a certain knowledge about the main fields of application of SEROX was available in the beginning of the 1990's already.
At that time, ALSA decided to focus the marketing of SEROX on alumina mass markets at first.

The first step of that way was to develop an alumina additive for the cement clinker production. Thereby, the main task was to achieve as well acceptable handling properties as a stable quality.

Those problems were solved by:

- feeding of the facilities with a stable pre-mix of input salt slag
- implementation of a strict quality monitoring system throughout the production
- improvement of the chloride washing to keep the chlorides below 0,5 %
- turning a muddy filter cake to a moist bulk ware of about 25 % moisture
- special treatment steps to lower the ammonia odor.

On that basis, ALSA was able to introduce their SEROX output into the cement clinker line between 1994 and 1998 nearly completely.

It turned out that SEROX can be used as an Alumina raw material like bauxite, clay etc. to introduce $Al_2O_3$ into the clinker burning process of the cement kiln.

There, the Alumina forms minerals like Calciumaluminateferrite (C4AF), Tricalciumaluminate (C3A) etc. The amount of alumina needed has to be figured out according to the cements modules of lime, silicate and alumina.

Due to its slight content of fluorspar SEROX can initiate the forming of the compound $11CaO*7Al_2O_3*CaF_2$ within the clinker. Furthermore, an additional input of Alumina by SEROX tends to lower the silicate modulus and to raise the C3A content.
As a result, SEROX can improve the sintering process as well as the early setting of the cement. That is why, the SEROX use leads to remarkable fuel savings of the kiln operation respectively raises the capacity of the kilns.

Usually, depending on the raw materials situation on site, the amount of SEROX added to a 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 more than 1,500,000 metric tons of SEROX without any ecologically harmful impact on the environment.

## 4.2. Mineral wool

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

At that time, ALSA was successful in convincing one of the leading mineral wool producers to start tests with SEROX as a substitute of bauxite.

The following table shows the range of chemical compositions of mineral wool fibres (3):

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

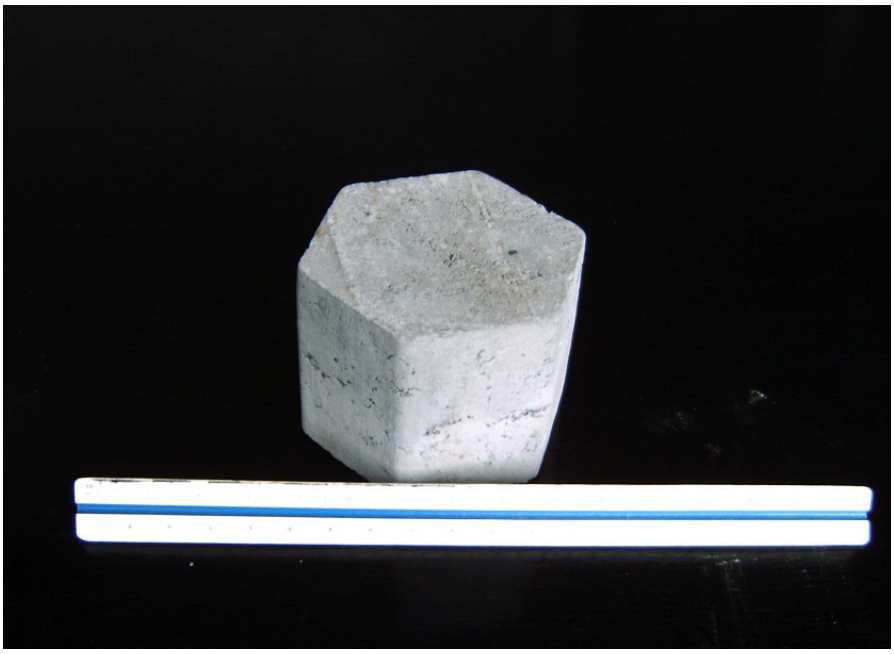
| | |
|---|---|
| $SiO_2$ | 38 – 46 |
| CaO | 15 – 38 |
| $Al_2O_3$ | 10 – 32 |
| MgO | 2 – 10 |
| FeO | 0.3 – 7 |
| $Na_2O$ | 0.3 – 3 |
| $K_2O$ | 0.3 –1.3 |

Non-carcinogenic rock wool fibres those are meeting the aforementioned EU directives specification usually range between 18 and 25 % $Al_2O_3$ content.

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

Thereby, in case of some need of additional Alumina for the input materials mix of a melting furnace, SEROX has simply to be added to the other raw materials, usually consisting of lumpy rock stones, slags, internal recycling materials etc., in a proper way.
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 (see picture 5).

Picture 5: SEROX-containing feed brick for a cupola melting furnace



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.

ALSA have been supplying successfully a couple of mineral wool works in Europe with more than 250,000 metric tons of SEROX since 1998. The SEROX consumption of the mineral wool line shows a considerably rising tendency.

## 5. second step - diversification and quality improvement

### 5.1. 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 parallely a permanent product improvement process. 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. 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.

ALSA have been increasing the SEROX-T output continuously.
In 2004, ALSA started their first SEROX drying facility at Becancour/Canada.
Furthermore, ALSA have been operating a second rotary drying facility for SEROX at Hannover since 2006 and is about to start-up a third one at Toeging/Germany.

Picture 6: 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

| Grain size (microns) | Mass pct. of screen underflow, typical |
|---|---|
| 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 Canadian subsidiary to blenders in the USA. There, the SEROX gets briquetted and forms 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.

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

5.2. 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) in 1995 to cement kilns.
Table 7 shows an example of such a pre-mix.

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

| | |
|---|---|
| $Al_2O_3$ | 43 |
| CaO | 2,5 |
| $SiO_2$ | 4 |
| MgO | 5 |
| $Fe_2O_3$ | 38 |
| $Na_2O+ K_2O$ | Max. 1 |
| Loss of ignition | 6 |

## 6. third step - further potential SEROX markets

On ALSA's development schedule, there is a couple of further potential applications. Most of them need a special pre-treatment of SEROX like calcination, pelletizing, briquetting, etc. In the following a short survey is to be given.

6.1. Ca-Aluminates

Calcium Aluminates are used as quick - setting high alumina cements or synthetic steel refining slags. To form the aluminate-minerals suited $Al_2O_3$-bearing materials (usually bauxite) have to be mixed with CaO containing materials (limestone, chalk, quick lime, etc.) and calcined or molten after that.

SEROX can be used as an Alumina raw material to introduce $Al_2O_3$ into the Ca-Aluminates producing process replacing bauxite partly or completely.

As secondary steel slags, calcium aluminate products made from SEROX show excellent melting properties. Furthermore, pre-sintered calcium aluminate slags made from SEROX are highly efficient in removing sulphur, phosphorus and aluminium oxide from molten steel. Steel grades with contents of sulphur between 0.003 and 0.005 % and phosphorus between 0.015 and 0.009 % have proven to be reachable.

Beside the said pre-molten or pre-sintered products simple mixings of dried or calcined SEROX with quick lime are able to do the same job in principle.

Thereby, it is favourable to make briquettes of SEROX and quick lime to avoid dust formation. At present, a steel mill of a well known and world wide operating steel group is already using SEROX containing pellets for slag conditioning purposes in

Europe. These pellets of SEROX are said to show excellent melting properties. Therefore, fluorspar could be replaced as a flux.

Furthermore, ALSA have carried out tests to produce high alumina cement clinkers succesfully and tested their properties.

ALSA would appreciate to find partners in developing a production of high alumina cement or secondary slag conditioner from SEROX.

### 6.2. Light weight construction materials

From SEROX, shaped as well as unshaped mineral foam products can be made if there is any demand for producing not flammable light building materials.

Thereby, according to an ALSA owned patent (4), SEROX must be treated in a flash calciner between 700 and 800 °C 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 proportions, the density of the light weight solid foam can be range from 0.4 to 0.8 metric tons per cubic meter.

### 6.3. Ceramics / Refractories

SEROX as well as calcined SEROX can be used as a high Alumina raw material like bauxite, Kyanite, Andalusite, Sillimanite, fire clay etc. for producing ceramics and refractories.
But, compared to high grade alumina, remarkable contents of magnesia, silica and lime of SEROX have to be taken into account.

Nevertheless, calcined or dried SEROX is expected to be able to partly replace bauxite in a couple of utilizations at least (5).

SEROX is said also to be able to introduce alumina into sanitary ware. Here, SEROX could again be used to raise the alumina content of raw material mixtures of ceramic tiles for example. Thereby, replacing quartz, it is expected to create a higher strength of the bodies at faster firing.

ALSA conducted a bunch of investigations into the matter of ceramics and refractories. But, due to the huge variety of applications of that line on one hand, and to the special composition of SEROX on the other hand, ALSA is still searching for a co-operation partner to get a first application project into operation.

## 6.4. Aluminium electrolyses cells

The use of SEROX as a refractory material is expected to be especially suited in the branch of the Aluminium-smelters. Aluminium electrolysis cells bottom linings can be produced from SEROX for example. Those bottom linings have to stand a temperature of about 900 °C.

ALSA's trials with SEROX for refractory mixes and bricks for the lining of aluminium electrolysis reduction pots have shown a favourable resistance against infiltration by the cryolite melt (6).
ALSA's idea is, to use SEROX as a monolithic stamping consisting of a mixture of SEROX and clay (about 10 pct.) that was formed to pellets, briquettes or bricks. This shaped bodies should be pre-heated up to 700 °C to remove moisture and crystal water as well as to create a sufficient mechanical stability. After that, the product is suited to be stamped into the electrolysis reduction pots (7).

Here again, ALSA is still searching for a co-operation to get a first application project into operation.

## 6.5. Abrasives

Given by its way of formation, SEROX is a stable mix of different synthetic minerals like corundum, spinel, Al-hydroxide. All those minerals are alumina bearing but showing different hardness and abrasivity. Marketable high quality abrasives usually consist of exactly classified fractions of pure minerals like garnet or corundum e.g.

That is why, ALSA carried out a series of tests to form a mono-mineral abrasive material from SEROX.
Thereby, after being mixed with coke breeze and iron chips SEROX was molten in an arc furnace at around 2.000 °C. A molten spinel product of very promising abrasive properties was produced containing about 85 pct. of Alumina (8).

SEROX can also be molten as a pure material without any addition of other raw materials. Thereby, depending on its chemical composition (mainly on the Magnesia and Silica content) a product will be formed consisting mainly of alumina-enriched Mg-spinel or mixtures of corundum, spinel and a few other minor ingredients. Both minerals, corundum as well as spinel are well known abrasives of a Mohs hardness of 9 respectively 8.

That application requires considerably high production costs, and therefore hasn't been put into action so far.

## 6.6. Blast furnace feed

Blast furnaces usually need bauxite to introduce a certain level of alumina into the slag if said slags are supposed to be utilized for producing blast furnace cement. The consumption of a blast furnace is said to range from 25 to 40 Kg bauxite per metric ton of pig iron.

Here again SEROX could be used to replace bauxite.

To do that job, bricks or briquettes consisting of SEROX and cement, as already mentioned in the point mineral wool, would have to be formed.

## 6.7. Filler

Cement as well as concrete mortar mixtures usually contain varying proportions of different fillers for:
- improving the mechanical properties of the concrete
- saving costs by substitution of expensive cement.

Known fillers are fly ash, sand, silica fumes for example.

Due to its fineness (see point SEROX-T), dried SEROX also could be used as such a filler to be added to some mortar mix replacing up to 10 mass per cent of cement meal without any detrimental influence on the concretes strength. Thereby, considerable costs of cement could be saved.

Literature references (9) confirm that oxide products like SEROX can substitute sand up to 30 % and cement up to 10 %.

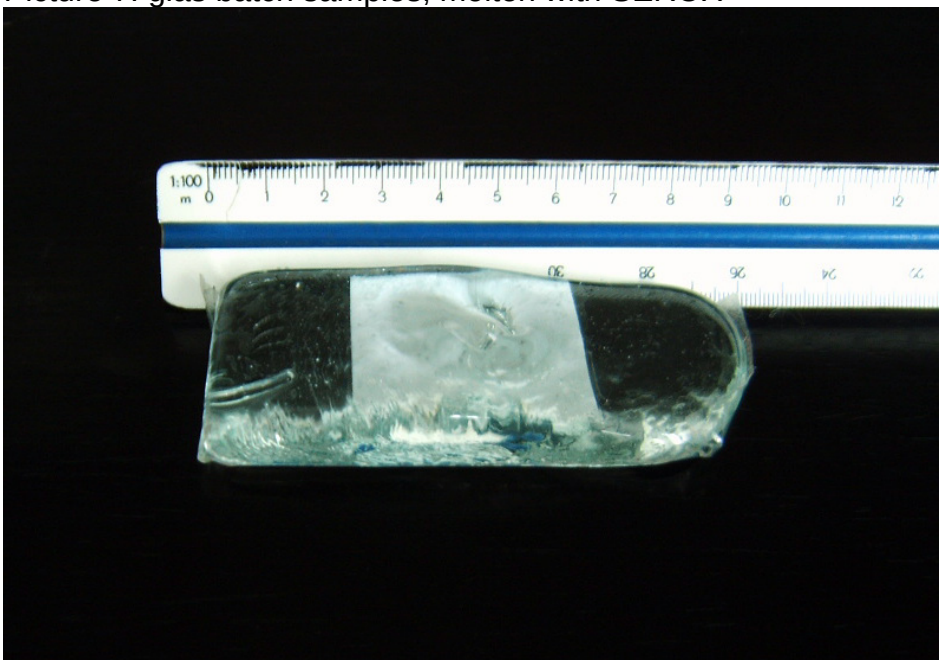
## 6.8. Glass

Since a couple of glass wares require a certain level of alumina, ALSA is about to investigate that new line of SEROX utilization.

First batch tests have shown that SEROX-T seems to be well suited to introduce alumina into glass without detrimental effects on the color. The molten glasses are expected to be suited even for float glass.

The tests are in an initial step of investigation and have to be continued.

Picture 7: glas batch samples, molten with SEROX



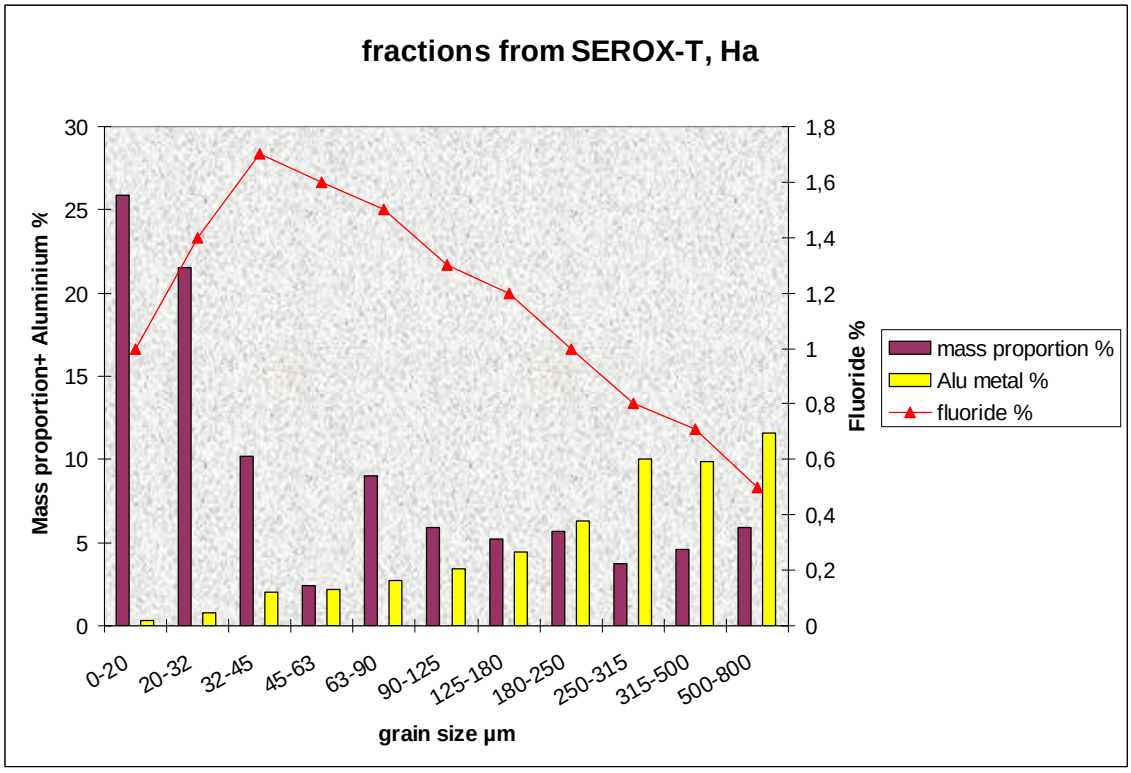

## 6.9. Special fractions from SEROX-T

It has been shown that fractions of determined properties can be produced easily from SEROX-T (10).

ALSA are working on a couple of special products made of SEROX-T. Those are for instance expected to be suited to the production of casting powder, porous concrete, fire resistant plastic fillers etc.
Interested partners from the due industrial branches are welcome to attend that investigations.

Picture 8 shows a grain size depending analysis of SEROX-T

Picture 8: grain size dependance of selected chemical components of SEROX-T




## 6.10. Calcined SEROX (SEROX-K)

When calcining SEROX above 1.000 degree Celcius, volatile components like fluorides and crystal water will be leaving the material. Thus, a product of raised alumina content occur as can be seen in table 13.

**Table 7**: typical composition of a SEROX calcinate from ALSA Germany

| Component | mass % |
|---|---|
| $Al_2O_3$ | 74 |
| CaO | 4 |
| $SiO_2$ | 9 |
| MgO | 9 |
| $Fe_2O_3$ | max. 2 |
| $Na_2O+K_2O$ | max. 2 |
| F | max. 0.1 |
| Loss of Ignition | 0 |

That line is still under development. The further development is depending on applications those are paying back the considerable calcination costs.

### 6.11. reclamation of Al-metal from SEROX

By a series of tests, ALSA showed already in 1992 that in principle even Aluminium metal could be recovered from SEROX.
The idea is to dissolve the alumina bearing minerals forming a sodium aluminate solution that can be introduced into the Bayer process prior to the step of the aluminium hydroxide precipitation.

A suitable way to achieve that was found by calcining a mix of SEROX and soda ash. Within the tests of ALSA, a sodium aluminate liquor could be leached from the calcined product, that is suited to the Bayer process. Thereby, more than 90 % of the available alumina were figured out to be recoverable from SEROX.

Facing the alumina markets rising prices and a partly unsupplied need of alumina, ALSA offer to carefully check that idea together with interested partners anew.

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