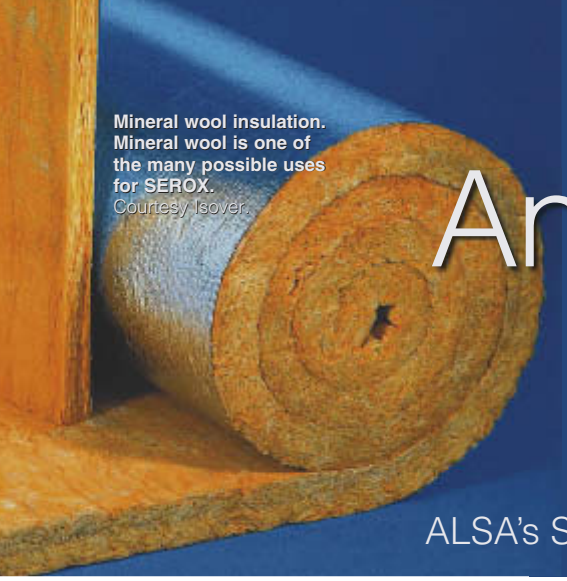

Mineral wool insulation. Mineral wool is one of the many possible uses for SEROX. Courtesy Isover.

An unconventional Al_2O_3 alternative

ALSA's SEROX range of recycled alumina-bearing raw materials

ALSA TECHNOLOGIES GmbH, a subsidiary of Germany's AGOR Group, produces and markets products recovered from the processing of aluminium salt slag; a residue generated during aluminium re-melting. The company has production sites in Germany and Canada. The Group operates two aluminium re-melting facilities in Canada.

These products can be used in a variety of industries as high grade secondary raw materials. The philosophy of AGOR is to develop "from a recycler to a producer", and aims to achieve this through intensified product marketing, together with market-orientated product development.

AGOR has a broad product portfolio, which includes an alternative source of alumina:

- SEROX: an alumina source for the cement and mineral wool industries, among others
- Aluminium granulate: secondary feedstock for aluminium products
- RESAL: melting salt for the secondary aluminium melting process and other applications
- Ammonium sulphate for the fertilisers industry

Producing SEROX

Despite their proven benefits in many applications, the short comings of conventional aluminas, notably bauxite, are undeniable. These products vary in composition and, hence, quality, while their availability is often an issue. SEROX, an industrially produced source of alumina, is now available to provide a viable alternative.

SEROX is a high grade alumina-bearing raw material containing about 66% Al_2O_3 (dry). *Tables 1* and *2* show the chemical and mineralogical characteristics of SEROX.

SEROX is produced on an industrial scale by ALSA. The location and production capacities for ALSA's present SEROX production plants (the company has one of the largest global production capacities for industrially produced alumina) is shown in *Table 3*.

SEROX supplied by ALSA's German operations at Hannover, Luenen and Toeging is available as three grades:

- SEROX moist: flowable fine and agglomerate material with a moisture content of about 25%
- SEROX-T: pumpable and free flowing dry product (max. 3% moisture), less than 1mm grain size
- FE-SEROX: flowable mixture of SEROX and iron oxide tailored to customer demand

These grades of SEROX can be shipped to customers 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

Utilising SEROX

SEROX offers many benefits, but its main advantages as an alternative source of alumina are a constant quality and, even more importantly, consistent availability. Unlike natural alumina-bearing raw materials sourced from international markets, SEROX offers reliable local supply and, thus, a secure source of alumina with a reasonable price structure.

As a result, SEROX has the potential to replace conventional alumina-bearing raw materials (eg. bauxite), and is well suited for the following end uses:

- cement clinker
- mineral wool
- synthetic calcium aluminates
- ceramics and refractory materials
- abrasives
- glass
- filler

The product can be mixed with other fine grained raw materials and/or binders to form pellets or bricks. 'Chunks' of SEROX can even be produced in briquetting machines.

The specific properties of SEROX usually contribute to energy cost savings for thermal processes by lowering the sintering or burning temperature required.

Table 1. Chemical composition of SEROX (typical values of main constituents, % of dry mass)

Al_2O_3	66
CaO	3
SiO_2	10
MgO	7
$Na_2O + K_2O$	1.5
Loss on ignition	10

Table 2. Mineralogical composition of SEROX (main constituents, minimum to maximum range)

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%

Table 3. ALSA Technologies' SEROX production capacity (tpa dry basis)

Hannover, Germany	65,000
Luenen, Germany	105,000
Toeging, Germany	50,000 (from 2007)
Becancour, Canada	25,000

Not only has this feature made SEROX a sought-after alumina resource for cement clinker, it can also be used by mineral wool producing companies.

Several tried and tested end uses for SEROX are discussed below.

Portland cement

All cements need to contain a certain amount of alumina in order to form minerals such as calcium aluminate ferrite (C_4AF) and tricalcium aluminate (C_3A), and the amount of alumina required varies according to the cement type.

SEROX can be used as a raw material to introduce Al_2O_3 into the clinker burning process of the cement kiln.

Due to its small fluorspar content, SEROX can initiate the formation of the compound $11CaO{\cdot}7Al_2O_3{\cdot}CaF_2$ within the clinker. Furthermore, this additional input of alumina tends to lower the silicate modulus and to raise the C_3A content. Consequently, SEROX can improve the sintering process as well as the early setting of the cement. It is this improvement to the sintering process that leads to fuel savings during kiln operation.

In addition, when feeding moist SEROX into the kiln process at the correct position, nitrogen oxide (NO_x) emissions can be reduced.

The amount of SEROX added to a cement kiln feed ranges 1-3% mass of the total input. However, this varies according to the total raw materials used.

ALSA has successfully supplied cement kilns in Europe and North America with more than 1.5m. tonnes (bulk) SEROX for over 10 years, without a harmful environmental impact.

Mineral wool

The European Commission's (EC) Directive 97/69/EC of 1997 classified certain mineral wools containing more than 18% alkaline and earth alkaline oxides as potential carcinogens.

Non-carcinogen rock wool fibres that meet the Directive's specifications usually contain 18-25% Al_2O_3.

The mineral wool producing process requires an appropriate level of alumina (*see IM August '06, p.36*). *Table 4* shows the chemical composition of mineral wool fibres.

SEROX is a suitable raw material for supplying alumina to these products. If additional alumina is needed in the raw materials mix in the melting furnace, SEROX can simply be added to the other feed materials.

A proven method of introducing SEROX into the furnace is to mix it with the other input material fines and recycled fibre waste, and form the mixture into bricks using cement, for example, as a binding agent.

Depending on the composition of the feed mix in the furnace and the chemical specifications of the desired mineral wool product, the SEROX content of the bricks usually ranges between 5-30% by weight. However, it can be raised to 80% if required.

The fluxing properties of SEROX can help to make energy cost savings by lowering the fuel consumption of cupola furnaces. The material appears to dissolves faster than bauxite in the cupolas melting bath.

Depending on the customer's needs and the feeding system technology used, ALSA offers moist SEROX, as well as dry SEROX-T to produce mineral wool.

The company supplied mineral wool operations in Europe with more than 250,000 tonnes of SEROX for more than eight years, and its consumption in mineral wool lines is growing.

Ca-aluminates

Calcium aluminates are used as quick-setting high alumina cements or synthetic steel refining slags.

In order to produce these aluminates, suitable Al_2O_3-bearing materials (usually bauxite) are mixed with CaO-containing materials (eg. limestone, chalk, and quick lime) and subsequently calcined. SEROX can also be used as an alternative source of alumina in these applications to either fully or partially replace bauxite.

When used as a synthetic steel slag, pre-sintered/pre-molten calcium aluminate slags usually melt more easily and faster than more common mixtures of calcined bauxite and burnt lime. Therefore, the purifying processes required in secondary metallurgy (eg. for ladles, ladle furnaces, casting tundishes) can be accelerated and superior steel grades can be produced.

Calcium aluminate materials manufactured using SEROX products that contain minor ingredients such as SiO_2 and MgO can further improve the melting behaviour by lowering the melting point.

Pre-sintered calcium aluminate slags produced using SEROX are highly efficient in removing sulphur, phosphorus and aluminium oxide from molten steel.

Reports on the desulphurisation and dephosphorisation properties of calcium aluminates made from SEROX (known as ALSAflux) in comparison with more commonly used market products are available from ALSA. Steel grades containing 0.003-0.005% sulphur and 0.015-0.009% phosphorus have been achieved using SEROX.

In order to produce Ca-aluminate slags, SEROX is mixed with ground lime, then pelletised, and calcined at about 1,250°C. As a result, mainly aluminates of the $C_{12}A_7$ type (mayenite) are produced.

Depending on the application for which the calcium aluminate slag will be used, the amount of alumina introduced by SEROX can be tailor-made to 35-70% (*see Table 5*).

Dried or calcined SEROX mixed with quick lime is able, in principle, to perform the same function as pre-molten or pre-sintered products. It can be favourable to make briquettes of SEROX and quick lime in order to avoid dust formation.

Via its Canadian subsidiary, ALSA is currently supplying coarse SEROX (+1mm) to blenders in the USA. These blenders

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

Table 5. Composition of aluminate slags made from SEROX (% by weight)

Lime:alumina	50:36 (high lime)	42:42	40:43	30:51	10:70 (high alumina)
Al_2O_3	35.9	42.3	43.3	51.6	69.3
CaO	50.5	42.3	39.1	30.0	9.9
Fe_2O	1.1	1.1	1.2	1.3	1.5
SiO_2	4.8	5.4	5.8	6.4	8
MgO	5.2	6.0	6.4	7.1	9
Na_2O+K_2O	1.1	1.3	1.3	1.4	1.8
TiO_2	0.2	0.3	0.3	0.4	0.5
F	<0.5	<0.5	<0.5	<0.5	0.1

Table 6. Analysis of high alumina cement clinker using SEROX (% by mass)

Al_2O_3	47-52
CaO	28-38
MgO	4-7
SiO_2	6-8

Table 7. Composition of a raw material mixture for sulpho-aluminate cement using SEROX (mass %)

SEROX	42
Limestone	42
Gypsum	16

Table 8. Chemical analysis of refractory spinel and cordierite made from SEROX (% by mass)

	Cordierite	Spinel
Al_2O_3	32	58
CaO	2	4
MgO	13	24
SiO_2	50	11

use SEROX as part of a mixture of quick lime and alumina for steel mill secondary metallurgy.

In order to produce quick-setting alumina cements using SEROX it is recommended that the raw material (ie. SEROX with limestone or chalk) be pelletised prior to calcination at a temperature of about 1,350°C.

This mixture should comply with the clinker chemical composition shown in *Table 6*.

If the chemical range outlined in *Table 6* is achieved, a clinker containing up to 50% aluminates of the type Ca ($CaO{\cdot}Al_2O_3$) and Ca_2 ($CaO{\cdot}2Al_2O_3$) can be formed. The lower the silica content of the clinker, the better the product quality will be.

ALSA has successfully carried out pilot tests to produce calcium aluminate cement clinkers. The company owns a process patent for the production of aluminate cement clinker using SEROX.

In Germany, the quick-setting cement market is highly competitive and demands precise, high quality specifications. ALSA aims to find partners outside Europe in order to develop an alumina cement production project based on SEROX.

In addition to this, a special, quick-setting and swelling cement can be made by utilising SEROX by adding gypsum to a raw material mix (*see Table 7*).

By calcining this mixture at between 1,100°C and 1,300°C a material can be produced that contains about 70% of the hydraulic-setting mineral $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$.

Lightweight construction

Mineral-based foams are increasingly used for lightweight building materials. They are light and easy to handle, as well as providing insulation and fire resistance. Shaped and unshaped mineral foam products can be made using SEROX.

According to an ALSA-owned patent, for use in these applications SEROX must be flash calcined at 700-800°C, prior to being mixed with a liquid sodium silicate and other ingredients. This mixture is able to swell quickly and form a solid, stable mineral foam.

The solid foams made using SEROX are fire resistant to up to 1,000°C, and can easily be shaped by cutting after hardening.

Depending on which ingredients are used in this mixture (eg. fillers like cement, burnt lime, dry SEROX-T) and their proportions, the density of the lightweight solid foam can range 0.4-0.8 tonnes per cubic metre.

Ceramics/refractories

Refractories are high temperature-resistant ceramic products formed as bricks or monolithic products, made from raw materials such as alumina, corundum, mullite, spinel, cordierite, and aluminate cement.

SEROX and calcined SEROX can be used as high alumina raw materials (to replace minerals such as bauxite, kyanite, andalusite, sillimanite, and fire clay) in ceramic and refractory production.

SEROX is a proven alumina raw material for refractory bricks and monolithics. Furthermore, SEROX can be utilised to raise the alumina content of clays in the production of grog. It can also be used for the production of refractory high alumina cements (*see calcium aluminates section above*).

SEROX-T also provides a suitable replacement for up to 25% of the relatively expensive high alumina cement used in refractory mortars.

ALSA has demonstrated that refractory minerals such as spinel or cordierite can be produced using SEROX. Pilot tests have been carried out to produce these raw materials for refractory brick and masses production. In order to achieve this, SEROX was mixed with sand and magnesia to produce cordierite, and only magnesia for spinel, prior to pelletisation of the mixture, and calcining of the pellets in a flash calcinator at 1,200°C. *Table 8* shows the chemical analysis of these products.

When used as a refractory raw material, SEROX can be especially advantageous in aluminium smelting. The bottom linings for aluminium electrolysis cells can be produced using SEROX. These linings have to withstand temperatures of about 900°C.

ALSA has trialled SEROX for use in the refractory mixes and bricks used in aluminium electrolysis reduction pot linings, and these have shown a favourable resistance to infiltration by the cryolite melt.

When used in monolithics, it is recommended that SEROX is mixed with clay (about 10%) and formed into pellets, briquettes, or bricks. These shaped bodies should be pre-heated up to 700°C to remove moisture and crystalline water, as well as to create the necessary mechanical stability. Following this, the material can be used in electrolysis reduction pots.

SEROX can also introduce alumina into sanitaryware and can be used to raise the alumina content of raw material mixtures used in ceramic tile production. As such, it can replace quartz and improve the strength of ceramic bodies during fast firing.

However, coarse grains (100-500μ) of SEROX, consisting for example of aluminium metal, are not suitable for these ceramic applications. Therefore, ALSA offers fine grades of SEROX-T to serve these end uses.

Abrasives

SEROX is a stable mix of different synthetic minerals (eg. corundum, spinel, Al hydroxide). All of these minerals are alumina-bearing, but they show different hardness and abrasiveness.

Marketable high quality abrasives usually consist of closely classified fractions of pure minerals such as garnet or corundum. This is why ALSA performed a series of tests to produce a mono-mineral abrasive material using SEROX.

This was done by mixing SEROX with coke breeze and iron chips and melting the mixture in an electric arc furnace at

around 2,000°C. A molten spinel product was produced with promising abrasive properties and containing about 85% alumina.

Pure molten SEROX, without any addition of other raw materials can also be utilised. Depending on its chemical composition (principally its magnesia and silica content), a product can be produced consisting mainly of alumina-enriched magnesia-spinel or mixtures of corundum, spinel, and other minor ingredients. Both corundum and spinel are well known abrasives with a Mohs' hardness of 9 and 8 respectively.

Blast furnace feed

If a slag is required to produce blast furnace cement, and the slag needs additional alumina, then bauxite is usually added. Consumption bauxite in this application is estimated at 25-40kg per tonne of pig iron produced.

Once again, SEROX can be used in this application as a replacement for bauxite.

Filler

Cements, as well as concrete mortar mixtures, usually contain varying proportions of different fillers in order to:

- improve the mechanical properties of the concrete
- provide cost savings by substitution of expensive cement materials

Established fillers used in this sector are fly ash, sand, and fumed silica. Due to its fineness, dried SEROX can also be used as a filler in some mortar mixes to replace up to 10% by mass of the relatively expensive cement meal, without any detrimental effect on the strength of the concrete. Oxide products such as SEROX can be used to substitute sand by up to 30% and cement by up to 10%.

ALSA believes that very fine fractions of SEROX-T can achieve a cement replacement of more than 10 %. Meanwhile, fine fractions of SEROX-T can strengthen the mechanical structure of the concrete. As a result, these SEROX grades could be blended with the cement meal as an additive.

SEROX has been successfully used as a filler in concrete mortar production in France for the past two years.

Glass

Certain glassware products require the addition of alumina in their production processes, and these end uses represent a new opportunity for ALSA and SEROX.

Alumina improves the chemical stability of the glass, and usually glasses contain between 0.5-2% alumina. Special glasses can contain up to 20% alumina. Usually, the appropriate level of alumina is introduced into the raw material mix via feldspar concentrates, aluminium hydroxide, nepheline syenite, or china clay.

Initial batch testing has shown that SEROX-T is well suited as an alumina for glass, without detrimentally affecting the colour of the glass.

During the tests, SEROX-T was able to replace nepheline syenite as a raw material. The composition of the batch mix for container glass used in the tests can be seen in *Table 9*.

SEROX-T

ALSA started up its first SEROX drying facility at Becancour inCanada in 2004.

ALSA is increasing its output of SEROX-T (a dry grade of SEROX), as it offers good handling properties and can be used in several industrial applications. For example, the company has been operating a second rotary drying facility for SEROX at Hannover, Germany since November 2006, and is about to start-up a third one at Toeging, Germany.

SEROX-T is chemically identical to moist SEROX (*see Table 1*).

At present, ALSA is working on a couple of special products made from SEROX-T. These are intended for use in the production of casting powder, porous concrete, and fire resistant plastic fillers.

In conclusion

SEROX is an unconventional high alumina product with great potential for applications such as cement clinker, mineral wool, calcium aluminates, ceramics, glass, as a filler.

Buoyant raw material prices and a tightness in alumina supply, has allowed ALSA to offer different grades of SEROX based on its steadily growing production capacity.

SEROX offers a safe source of high quality alumina raw materials of reliable availability and at a reasonable price.

Table 9. A glass batch mix containing SEROX (mass % of batch components)

Silica sand	60
SEROX-T	1.4
Soda ash	18.4
Lime	9.5
Dolomite	9.7
Sodium sulphate	0.9
Carbon	0.1

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