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Raw Materials for Production of SrAC

1. Raw Materials and Raw Material Treatment

For the synthesis of strontium aluminate cement it is necessary to find the proper source of strontium (SrO) and aluminium oxide (Al_2O_3).

Two major strontium minerals are its carbonate, strontianite (SrCO_3) and more abundant sulfate mineral celestite (SrSO_4). William Cruickshank in 1787 and Adair Crawford in 1790 independently detected strontium in the strontianite mineral, small quantities of which are associated with calcium and barium minerals. They determined that the strontianite was an entirely new mineral and was different from barite and other barium minerals known in those times. In 1808, Sir Humphry Davy isolated strontium by the electrolysis of a mixture of moist strontium hydroxide or chloride with mercuric oxide, using mercury cathode. The element was named after the town Strontian in Scotland where the mineral strontianite was found [91].

The **strontium oxide** (SrO) is the first substantial component of strontium aluminate clinker. Therefore, the strontium carbonate (SrCO_3) is the most appropriate input material for the synthesis of strontium aluminate clinker. In nature SrCO_3 occurs as rare orthorhombic mineral **strontianite**¹ (space group *Pcmm*) and together with isostructural minerals aragonite (CaCO_3), witherite (BaCO_3) and cerussite (PbCO_3) it belongs to anhydrous carbonates from the group of aragonite² [92,93].

The structure of strontianite (Fig.1(a)) is based on isolated $[\text{CO}_3]^{2-}$ triangles which are placed in layers perpendicular to *c*-axis. The layer has two structural planes where $[\text{CO}_3]^{2-}$ ions are oriented in the opposite direction. Cations with the coordination number of 9 are placed between these layers.

Natural and artificially synthesized binary (**aragonites** up to 14 mol. % Sr [94], **strontianites** up to 27 % Ca [94], **witherites** [94], **baritocalcites** [95]) or ternary solid-solutions (**alstonites** [94]) of these carbonates are intensively studied in order to elucidate the mechanism of their formation, their structure, the thermodynamic stability and the luminescence properties.

1 Discovered in 1787 (Strontian, Scotland). Originally was considered the barium bearing mineral; which was disproved by Crawford and later by Klaproth and Kopp. Named in 1791 by Friedrich Gabriel Sulzer after the locality Strontian in Scotland.

2 There are three main groups of anhydrous carbonates without additional anions. The group of calcite (trigonal, space group $R\bar{3}c$, $A = \text{Ca, Mg, Mn, Fe, Co, Ni, Zn and Cd}$) and aragonite (orthorhombic, space group *Pmnc*, $A = \text{Ca, Sr, Ba and Pb}$) has the composition given by general formula ACO_3 . The trigonal group of dolomite (space group $R\bar{3}$ where $A = \text{Ca}$ and $B = \text{Mg, Fe, Mn and Zn}$) has general composition given by the general formula $\text{AB}(\text{CO}_3)_2$.

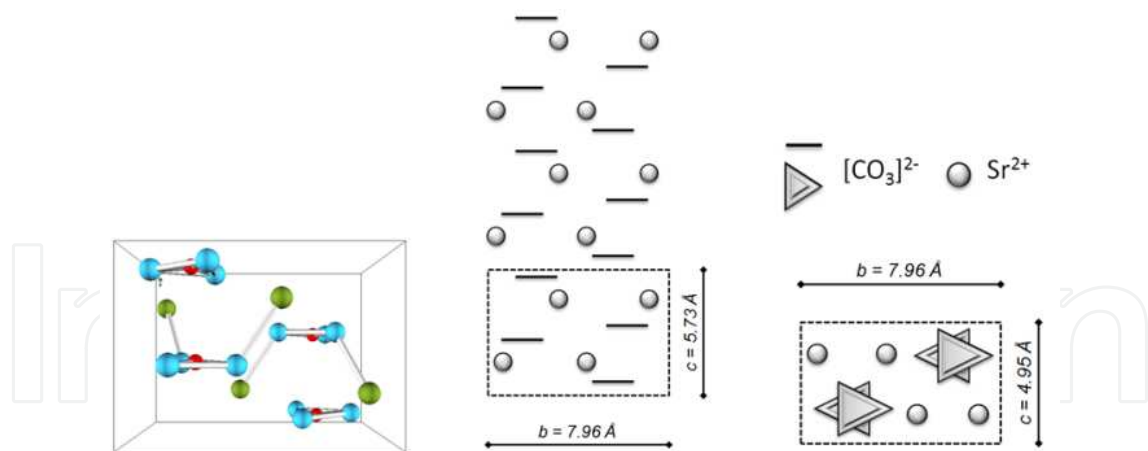


Figure 1. Structure of strontianite consists of isolated $[\text{CO}_3]^{2-}$ triangles arranged into layers with Sr^{2+} ions in the space between layers.

Calcium carbonate minerals include considerable amount of strontium from seawater as they precipitate. It stands to reason that the solid-solutions of strontianite with calcite and aragonite ($\text{Ca}_x\text{Sr}_{1-x}\text{CO}_3$) are the most explored. There is an immiscibility gap in the range 0.12 (aragonites) $< x < 0.87$ (strontianites) under ambient conditions, which disappears at the temperature of $\sim 107^\circ\text{C}$ [92,94,96,97-100].

Therefore natural sources of SrCO_3 are rare and have no industrial importance, strontium carbonate as well as other compounds such as strontium nitrate, strontium oxide and chloride are prepared from the orthorhombic mineral **celestite**³ (SrSO_4 , space group $Pnma$ with cell unit parameters $a=8.359\text{ \AA}$, $b=5.352\text{ \AA}$, $c=6.686\text{ \AA}$ and $Z=4$) using the techniques described in Chapter 2.1.1. The structure of celestite consists of isolated $[\text{SO}_4]^{2-}$ tetrahedrons and Sr^{2+} ions (Fig.2).

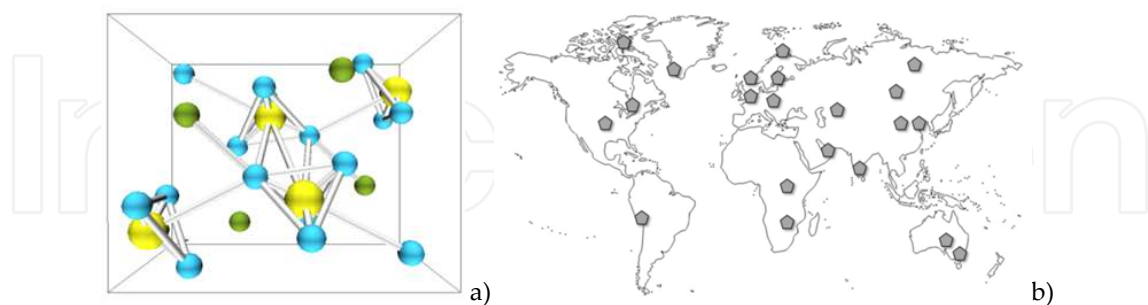


Figure 2. Structure of celestite (a) and distribution of large celestite deposits in the world (b).

Celestite together with isostructural barite (BaSO_4) and anglesite (PbSO_4) belong to anhydrous sulfates from the group of barite⁴. Similarly to the solid solutions of carbonates men-

³ Discovered in 1791 and named in 1799 by Abraham Gottlieb Werner from the Greek "cœlestis," for celestial, in allusion to the faint blue color of the original specimen.

tioned above, also celestite and barite (BaSO_4) coexist in the marine environment with significant fractions of Sr and Ba in solid solutions. Therefore it is better to identify barite suspended in seawater as the strontian barite ($\text{Sr}_x\text{Ba}_{1-x}\text{SO}_4$) [101].

The second substantial component of strontium aluminate cement is **aluminium oxide** (Al_2O_3). The most stable crystalline form of Al_2O_3 is the polymorphic modification of hexagonal corundum ($\alpha\text{-Al}_2\text{O}_3$) from the $R\bar{3}C$ space group⁵. The crystal structure of corundum type is typical for other oxides, such as **hematite** (Fe_2O_3), **eskolaite** (Cr_2O_3), **karelianite** (V_2O_3) and **tistarite** (Ti_2O_3). Therefore, naturally occurring minerals are often colored by the admixture of these elements, e.g. ruby is red colored by Cr and blue sapphire by Fe and Ti. That means that these elements are also interesting from the point of view of modification the properties (course of sintering, hydration and setting) of strontium aluminate cement. Chapters 4 and 5 are dedicated to this topic [424].

Pure aluminium oxide is relatively rare, but single crystals of gemstones such as sapphire (colorless) or ruby (red due to the content of chromium) can be found in nature [424]. Industrial production of Al_2O_3 is based on the Bayer process of bauxite. The main part of produced alumina is used in metal industry for the production of aluminium by Hall-Heroult Process [102-105].

The application of Al_2O_3 in ceramics includes the production of alumina porcelain and alumina oxide ceramics, ZTA (Zirconia Toughened Alumina) ceramics and the applications such as electroceramics, construction ceramics, shaped and unshaped refractory products, abrasive materials, etc [106-112]. From the point of view of the volume of production, polycrystalline alumina is the most frequently used material as ceramics for the structural applications. However, in comparison with for example, silicon nitride (Chapter 6), where the influence of various additives on the microstructure and properties is well characterized and understood, alumina remains the material with many unknown factors yet to be revealed. Alumina based materials can be roughly divided into three groups [424]:

- **Solid-state sintered aluminas:** enable to prepare nanocrystalline materials with excellent mechanical properties and well-sintered ceramics being transparent to visible light [113,114].
- **Liquid-phase sintered aluminas (LPS):** are substantial part of industrially produced alumina-based materials. Silica, alkali oxides and oxides of alkali earth metals are used as sintering additives [115-117].
- **Alumina-based composites:** ZTA and alumina based nanocomposites with non-oxide phases such as SiC or TiC [118-123].

The preparation of Al_2O_3 mono-crystals is based on **Verneuil process** consisting in the flame fusion in high temperature region from 1500 to 2500 °C [124-127]. Bauxite (Fig.3) is also used

4 Barite – celestite series from the group of barite. Anhydrous sulfates without additional anions with the composition given by general formula ASO_4 , where A = Pb, Ba, Sr.

5 Structure and lattice parameters of corundum are described in Chapter 4.1.

for the production of calcium aluminate cements [128] or is calcined and used as opening material for the refractory products [129-131].

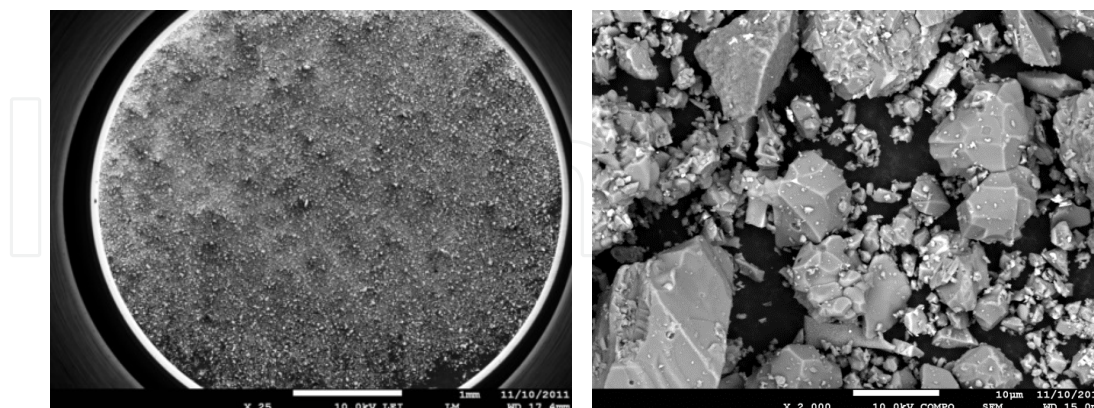


Figure 3. SEM image of calcined bauxite grain.

In order to obtain good quality in abrasive, refractory and pottery products, the content of impurities should be reduced. Chemical processes include the pyrochemical techniques, acid leaching methods or reductive dissolution alternatives. The pyrochemical techniques involve the treatment of bauxite at high temperature with gases such as H_2 , Cl_2 or anhydrous HCl [132,133]. The acid leaching methods are based on the application of strong inorganic acids such as HCl or H_2SO_4 [134-137].

A serious problem with these techniques is that leaching of iron is often accompanied by substantial co-dissolution of aluminium hydroxides, particularly during the treatment of gibbsitic and boehmitic ores. Selective dissolution of iron can be obtained applying mild reducing conditions. In this case the dissolution of $Fe(III)$ oxides takes place via the reduction of ferric iron to the divalent state. It is widely accepted that biological mechanisms are often involved in the mobilization of iron in natural systems. For the particular case of bauxites the biological activity of iron reducing microorganisms is most probably involved in the generation of gray-colored iron depleted bauxites [138,139].

Since the production of alumina from bauxite ores consumes large amount of caustic soda, and generates large amount of “**red mud**” slurry waste, the alternative processes for the production of aluminium and aluminosilicates via carbothermic reduction of bauxite ores was investigated. The reduction sequence of metal oxides in bauxite ores is iron oxides then silica and titania and then alumina (Fig.4). Metallic iron is formed at the temperatures below $1100\text{ }^{\circ}C$. At $1200\text{ }^{\circ}C$ or above the ferroalloy phase with silicon and aluminium is formed. Carbides of titanium, silicon and aluminium were formed by the carbothermal reduction. The metals were formed and dissolved in the ferroalloy phase, which after saturation, was segregated as metal carbides distributed inside the alloy phase as inclusions or around the alloy particles [140,141].

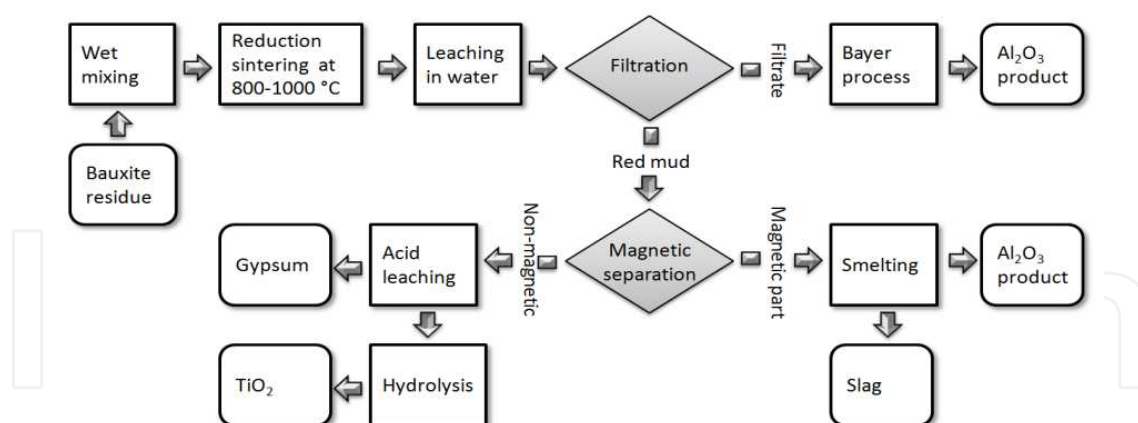


Figure 4. Process suggested for simultaneous recovery of iron, aluminium and titanium from red mud [146].

The utilization of Bayer's process residues in the cement production is also studied. Previous works proposed a method of treating red mud with saturated $\text{Ca}(\text{OH})_2$ solution followed by 3% H_2SO_4 , in order to remove Na. After heating, the treated material is suggested for the application in cement manufacturing. The major parts of red mud are hematite and alumina-rich phases (Fig.7), participating in the production of hydraulic crystal phases C_3A and C_4AF . Fe-rich waste could be then used for the production of sulphate resistant cements [142]. Other option includes the applications such as catalysts and adsorbents, ceramics, coatings and pigments, waste water and gas treatment, recovery of major and minor metals [143-146].

Bayer suggested that [143]: "Red, iron-containing residue, that occurs after digestion, settles well and, with sufficient practice, can be filtered and washed. Due to its high iron content and low aluminium oxide content, it can be, in an appropriate manner, treated or melted with other iron ores to iron". The concept of bauxite residue as an iron resource was tested by a number of workers over the intervening 120 years, however, the "appropriate manner" of treatment remains elusive [144].

The aluminium gels, salts (sulphates, nitrates or chlorides) or alkoxides and advanced ceramic fabrication techniques can be applied for the preparation of high purity products (please referee to Chapter 9). Bauxite is the mixture of aluminium hydroxides and oxyhydroxides such as boehmite, diaspore and gibbsite, with varying content of admixture minerals. Goethite, lepidocrocite, hematite, magnetite, kaolinite, chlorites, calcite, anatase, phosphates, etc are the major ones [148].

Bauxite, as the primary source of aluminum, represents a typical accumulation of weathered continental crust [147,148]. Bauxites are usually considered to be of three major genetic types [149-152]:

1. **Lateric bauxites** (sometimes called equatorial) are formed from weathered primary aluminosilicate rocks in equatorial climates comprising ~90% of the world's exploitable bauxite reserves. Lateritic bauxite is generally formed by in-situ lateritization, therefore, the most important factors in determining the extent and grade of it are thought to be

the parent rock composition, climate, topography, drainage, groundwater chemistry and movement, location of water table, microbial activity, and the duration of weathering processes.

2. **Sedimentary bauxites** are primarily formed by the accumulation of lateritic bauxite deposits during the mechanical transportation of surface flows. In addition, the consequent weathering and transfer of Al and Fe play substantial roles in bauxitization, which not only supports the formation of bauxite from kaolin clays but also refines the primary clastic ores.
3. **Karst bauxites** are named for their confinement to karst zones with karstified or karstifying carbonate rocks. Karst-type deposits originate from a variety of different materials, depending on the source area.

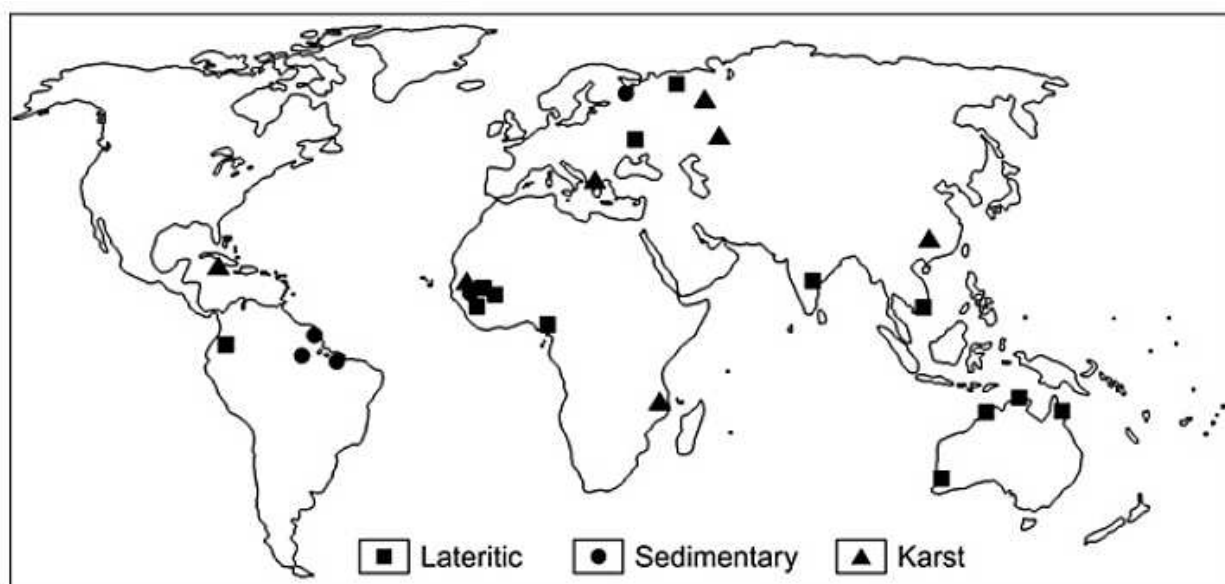


Figure 5. Distribution of superlarge bauxite deposits worldwide [152].

Each genetic group of bauxite experienced the separation of aluminum (Al) and silicon (Si) by the accumulation of Al, and the removal of Si, alkali metals, and rare earth elements from parent rock (sediment) during its weathering [148].

Bauxite deposits (Fig.5) form mainly at ambient pressure and temperature on the (sub)surface of continents. Abundant bioavailable irons, nutrient elements, sulfurs, and organic carbons make bauxite suitable for microorganisms to inhabit so they become rare geological sites that can preserve records of microbiological activity on the surface of continents under strong weathering effects. The microorganism activities can produce a family of minerals with special morphologies and stable isotope compositions. Bauxite deposits were studied in detail because of their economic value. They play an important role in the study of paleoclimate and paleogeography of continents because they contain scarce records of weathering and evolution of continental surfaces [148].

1.1. Industrial and laboratory production of SrCO_3

Chemical industry consumes over 95 % mined celestite for the conversion to other strontium compounds. The main admixtures in celestite ores are calcite (CaCO_3), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), quartz (SiO_2) and clay minerals. The gravity separation techniques and the flotation⁶ are mostly used for the separation of those admixtures due to high efficiency and low operating costs. Moreover, the process does not require the usage of other chemicals for the purification and has low environmental impact. On the other hand, the efficiency of these techniques for the preparation of celestite concentrate depends on the texture of ore as well as the type and quantity of associated impurities [153-155]. The particle size is other most important factor. Extremely fine particle sizes must be achieved by grinding in order to release celestite and calcite [156]. The difference in grindabilities makes it possible to separate celestite from gypsum by differential grinding [157].

The shear flocculation⁷ of fine celestite suspension with sodium dodecyl sulfate (SDS, $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$) or with anionic alkyl succinate surfactant can be performed in broad pH range (3 – 11) but the highest efficiency is reached at pH 7. Increasing concentration of surfactant has positive effect on the course of process. The most common inorganic dispersants used are sodium silicate, sodium phosphate and sodium polyphosphate. The investigation of mutual influence of additives shows that sodium silicate strongly prevents celestite with sodium dodecyl sulfate from shear flocculation, but the dispersive effect of SDS is low when anionic alkyl succinate surfactant is used. In the presence of sodium polyphosphate, the shear flocculation of celestite suspension increases slowly for both surfactants. The similar increase can also be observed for sodium phosphate in the presence of SDS. However, sodium phosphate dispersed the celestite suspension in the presence of anionic alkyl succinate surfactant [158]. Sodiumoleate (cis-9-Octadecenoic acid sodium salt) and tallow amine acetate (TAA) were more effective for celestite suspensions in the pH ranges 7–11 and 6–10, respectively [159].

The surface of celestite becomes hydrophobic by the adsorption of dodecyl sulfate on the surface. Sodium dodecyl sulfate is also effective for the flotation of celestite in the solution free of carbonate species over the broad pH range of 3-11. The surface transformation of celestite to strontium carbonate which takes place at $\text{pH} \geq 7.8$ causes that the zeta potential of celestite begins to be more negative and subsequently resembles that of strontium carbonate. Sulfate ions are exchanged by carbonate ions in the celestite crystal lattice, so CO_3^{2-} and HCO_3^- species are probably responsible for the negative increase in zeta potential. The surface transformation of celestite to strontium carbonate has no effect on floatability up to the pH of 10. Once the pH is higher than 10, the concentration of CO_3^{2-} and HCO_3^- species in

⁶ Flotation is an industrial process for the treatment of raw materials. The constituents of fine powdered raw materials are separated from the mixture according to the different wettability of individual solid species. The foam flotation process uses the interaction of gas bubbles with suspended material, which is next concentrated on the liquid level as foam.

⁷ Flocculation is a special case of coagulation where suspended particles of colloids form flake-like aggregates spontaneously or after the addition of clarifying agents.

aqueous solution is very intrinsic and the decrease of floatability is probably caused by the absorption of these species on carbonated surface of celestite [155].

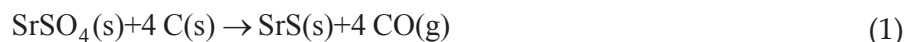
The coagulation and flocculation characteristics of celestite by inorganic salts, such as CaCl_2 , MgCl_2 and AlCl_3 , indicate that magnesium ion was more effective on the celestite suspension than calcium and aluminum ions at high pH levels. The effect varied significantly depending on the concentration. While calcium and magnesium ions were not effective for the suspension below neutral pH, aluminum ion caused the stabilization of the celestite suspension at these pH levels [160].

In general, the aggregation of fine particles can be achieved by neutralizing the electrical charge of interacting particles by coagulation, or flocculation can be carried out by crosslinking the particles with polymolecules [161]. The pH of isoelectric point of celestite determined by the hindered settling technique is 2.6 [160].

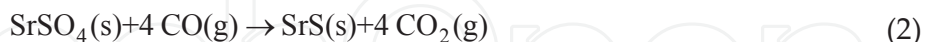
There are two basic processes to produce SrCO_3 from SrSO_4 [162]:

- a. Pyro-hydrometallurgical process or black ash method;
- b. Hydro metallurgical process.

The “**pyro-hydrometallurgical process or black ash method**” is first of them. Celestite is carbothermically reduced to water soluble sulphide (SrS), which is next dissolved in hot water⁸ The first solid-state reaction during the carbothermic reduction takes place at up to 400 °C [163]:



After the formation of surface layer of the product the further progress of reaction 1 is inhibited. Formed carbon dioxide diffuses through the layer and reacts with celestite according to the following reaction:



Carbon dioxide diffuses further out of reaction zone and generates more CO according to the Boudouard reaction if the temperature is ≥ 720 °C:



That means that direct reaction of celestite with carbon (Eq.1) has little importance and SrSO_4 can be transformed to SrS at the temperature higher than equilibrium of **Boudouard reaction**. The important factor of the process 2 is the reduction potential of gas phase given

⁸ Strontium salt can be then prepared directly by dissolving SrS in acid.

by the partial pressure ratio of $p_{\text{CO}}/p_{\text{CO}_2}$. It was also observed that the rate of carbothermic reduction significantly increases if celestite concentrate and carbon are milled together. The temperatures in the range from 1100 to 1300 °C with the excess of metallurgical grade coke are necessary to produce water-soluble strontium sulfide.

The dissolution of strontium sulfide in hot water can be expressed by the following heterogeneous reaction [164]:



Eq.4 shows that the pH of leaching solution increases from almost neutral to the value of 11.5 – 12.5 as the concentration of OH^- ions increases. Extremely high pH values ($\text{pH} > 14$) should be avoided in order to prevent the system from the precipitation of strontium hydroxide⁹:



The value of equilibrium constant K at 25 °C is $3.55 \cdot 10^{-29}$, i.e. $\log K = -28.45$. Therefore, the concentration of Sr(OH)_2 in leaching solution (Fig.6) can be expressed as:

$$\log_{10} [\text{Sr}^{2+}] = 28.45 - 2 \text{ pH} \quad (6)$$

That means that leaching of SrS must be carried out in relatively low alkaline medium in order to ensure high concentration of strontium in the solution. The solubility of strontium hydroxide is enhanced by increased temperature. Therefore leaching and precipitation of SrCO_3 at higher temperatures mean that the formation of Sr(OH)_2 precipitates is reduced.

On the other hand, leaching at $\text{pH} < 7$ generates hydrogen sulphide gas:



The generation of hydrogen sulphide gas takes place in early stages of leaching when the pH of slurry is relatively low.

Introducing the carbon dioxide gas or carbonating agent such as soda ash leads to the precipitation of strontium carbonate from supersaturated solution (Eq.13). The sequence of reaction steps includes the dissolution of carbon dioxide in solution and *in situ* formation of carbonic acid (H_2CO_3 , Eq.8), the dissociation of H_2CO_3 (Eq.9 with the equilibrium constant

⁹ $\text{Sr(OH)}_2 \cdot 8\text{H}_2\text{O}$ precipitates during cooling of hot supersaturated solutions. Strontium hydroxide octahydrate transforms to monohydrate by ageing of the precipitate. Anhydrous hydroxide can be prepared via thermal treatment of the precipitate up to 100 °C.

(K') given by Eq.10), the dissociation of bicarbonate species (Eq.11 with the equilibrium constant (K'') given by Eq.12) and the precipitation of strontium carbonate (Eq.13 with the ion product (P) given by Eq.14) [163-165].



$$K' = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \quad (10)$$



$$K'' = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (12)$$



$$P = [\text{Sr}^{2+}][\text{CO}_3^{2-}] \quad (14)$$

The solubility of strontium carbonate is $5.6 \cdot 10^{-10}$ at the temperature of 25°C and decreases to $1.32 \cdot 10^{-10}$ at the temperature of 100°C . The hydrolysis reaction leads to alkaline character of aqueous solution of SrCO_3 .

Eqs.8-14 show that one mole of gaseous CO_2 is required for the precipitation of each mole of SrCO_3 . The concentration of CO_3^{2-} ions in leaching solution for given pH is expressed by the following law:

$$\log_{10}[\text{CO}_3^{2-}] = \log_{10}K'' + \text{pH} + \log_{10}[\text{HCO}_3^-] \quad (15)$$

If the pH of leaching solution is higher than 7, H^+ ions formed by the reaction 11 neutralizing OH^- anions are released during leaching of SrS (Eq.4).

In general, the black ash method is concluded to be more the more economical than other alternatives [165].

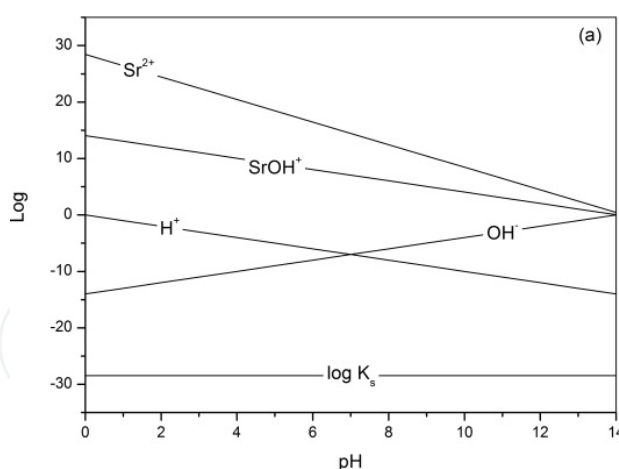
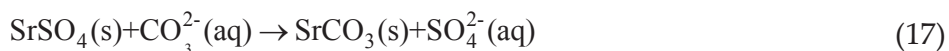


Figure 6. Influence of pH on the equilibrium concentration of Sr^{2+} and SrOH^+ ions in solution.

The second technique for the preparation of strontium carbonate is the **direct conversion method** or **hydrometallurgical method**. Strontium carbonate is prepared by introducing SrSO_4 powder into hot solution of Na_2CO_3 , where the following conversion process takes place:

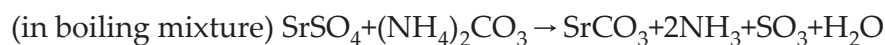
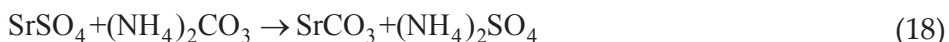


or better:

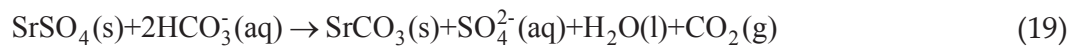


The effect of experimental conditions on the process includes the influence of temperature, solid to liquid ratio, particle size, stirring rate, Na_2CO_3 : SrSO_4 molar ratio, etc. The conversion rate of celestite to strontium carbonate increases with temperature up to 70 °C [165-170]. Prepared carbonate or sulphide is further converted to other strontium salts [91].

It is also possible to use ammonium carbonate $((\text{NH}_4)_2\text{CO}_3)^{10}$ and bicarbonate $(\text{NH}_4\text{HCO}_3)$ instead of soda ash for the conversion [165,171-174]:



¹⁰ Since NH_4^+ species as well as Na^+ ion in Eq.16 does not participate in the reaction, the same equation 17 will be obtained for both processes.



There is also an alternative in mechanochemical synthesis, where the mixture of SrSO_4 and NH_4HCO_3 is intensively milled. The soluble ammonium sulphate is next removed by leaching of the product in water [165].

Moreover lots of special techniques for the preparation of SrCO_3 were described in current literature. These methods include the preparation of strontium carbonate via solid-state decomposition route from inorganic precursor [746]. Simple solution techniques [175], solvothermal synthesis [176-178], refluxing method [188] hydrothermal synthesis [179-182], ultrasonic method or sonochemical-assisted synthesis [183,184], microwave assisted synthesis [185,186] and mechanochemical synthesis [168,187] were described. Depending on applied preparation technique, the strontium carbonate particles of different shape can be prepared, such as spheres, rods, whiskers and ellipsoids, needles, flowers, ribbons, wires, etc. [188].

The solubility of strontium salts is mostly either higher or lower than for corresponding calcium and barium salts (Table 1).

Cations	Ca ²⁺	Sr ²⁺	Ba ²⁺
Anions	Solubility [g•100 cm ⁻³]		
OH ⁻	0.160	0.810	3.890
F ⁻	0.0017	0.0175	0.1600
Cl ⁻	74.5	53.1	36.2
NO ₃ ²⁻	128.8	70.4	9.10
CO ₃ ²⁻	0.0014 (25 °C)	0.00155 (25 °C)	0.0022 (18 °C)
SO ₄ ²⁻	0.20	0.0148	0.00023
C ₂ O ₄ ²⁻	0.00058	0.0048	0.0125
CrO ₄ ²⁻	2.25	0.204	0.00037

Table 1. The solubility of salts of alkaline earth metals at the temperature of 20 °C.

Metallic strontium can be prepared by the electrolysis of mixed melt of strontium chloride and potassium chloride in a graphite crucible using iron rod as cathode. The upper cathode space is cooled and metallic strontium collects around cooled cathode and forms a stick. Metallic strontium can also be prepared by thermal reduction of its oxide with aluminum. Strontium oxide-aluminum mixture is heated at high temperature in vacuum. Strontium is collected by the distillation in vacuum. Strontium is also a reducing agent. It reduces oxides and halides of metals at elevated temperatures to the metallic form.

Strontium is also obtained by the reduction of its amalgam, hydride, and other salts. Amalgam is heated and the mercury is separated by the distillation. If hydride is used, it is heated at 1 000°C in vacuum for the decomposition and removal of hydrogen. Such thermal reductions yield high-purity metal which, when exposed to air, oxidizes to SrO. The metal is pyrophoric, both SrO and SrO₂ (strontium peroxide) are formed via ignition in air. When heated with chlorine gas or bromine vapor, strontium burns brightly, forming its halides (SrCl₂ or SrBr₂). When heated with sulfur, it forms sulfide (SrS) [91].

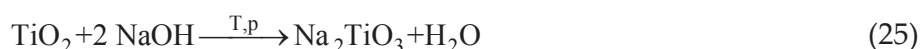
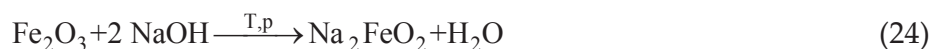
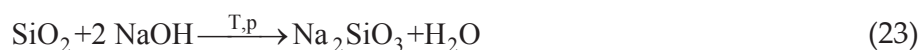
Strontium reacts vigorously with water and hydrochloric acid forming hydroxide Sr(OH)₂ or chloride (SrCl₂) with liberation of hydrogen [91]:



When heated under hydrogen it forms ionic hydride (SrH₂), a stable crystalline salt. Heating metallic Sr in a stream of nitrogen above 380°C forms nitride (Sr₃N₂).

1.2. Bayer process

Pure alumina, which is required for the production of aluminum by the Hall process, is made by the Bayer process [91]. The Bayer process was developed in 1887 by Carl Josef Bayer (1847-1904). It is the method for industrial production of aluminium oxide from bauxite. This method replaces earlier techniques developed by Henri Étienne Sainte-Claire Deville (1818-1881). Fine milled bauxite powder is leached in the solution of sodium hydroxide in autoclave under the temperature range from 160 to 250 °C and the pressure from 0.4 to 0.8 MPa. The basic components of bauxite are dissolved and soluble salts according to the following reaction scheme are formed [189]:



Significant amount of impurities which remains in the dissolved solid rest, so called “**red mud**” (Fig.7), is next separated from the solution by filtration¹¹. The IEP values vary with red mud ranging from 6.35 to 8.70 [347]. The liquid filtrate is then diluted so that the concentration of Al_2O_3 in the solution reaches the value of $150 \text{ kg Al}_2\text{O}_3 \cdot \text{m}^{-3}$ and the nuclei of $\text{Al}(\text{OH})_3$ are introduced [190].



The dilution means decreasing the pH of alkaline solution¹² and the precipitation of aluminium hydroxide. Precipitated gibbsite (Eq.27), which is the main product of Bayer process, is washed and calcined to Al_2O_3 in the rotary kiln (Eq.28).

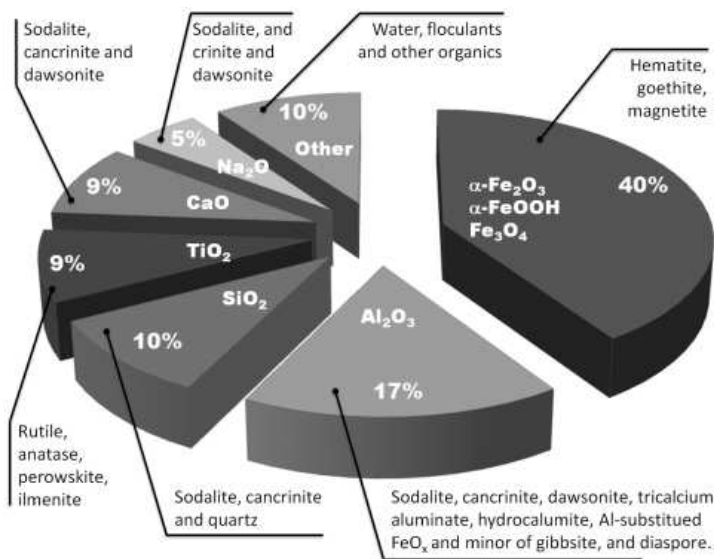
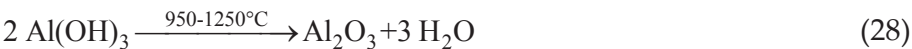
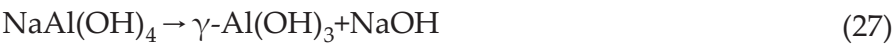


Figure 7. Composition of red mud [145].

The purity of prepared aluminium oxide is about 99.5 % and Na_2O is the main admixture in the product.



11 The deposition lagoon of red mud may be significant ecological load as was demonstrated by industrial accident in Hungary (Aika, 2010).

12 According to the definition law $\text{pH} = -\log [\text{H}_3\text{O}^+] = 14 - \text{pOH} = 14 - \log[\text{OH}^-]$, the teen times dilution causes the decrease of pH by 1.

The flowing diagram of the process is shown in Fig.9. For the applications where high content of α - Al_2O_3 is necessary, the mineralization is accelerated by AlF_3 (Eq.29). Several micrometer sized plate-like corundum crystals are formed.



Tricalcium aluminate hexahydrate (hydrogarnet) is used as a filter aid during the purification of sodium aluminate liquors. Furthermore, C_3AH_6 reduces the TiO_2 content of precipitated gibbsite and the formation of hydrogarnet at high-temperature (250°C) leaching minimizes the soda content of red-mud waste [191,192].

Fig.8 reveals that aluminium hydroxide can precipitate from the solution by introducing the carbon dioxide gas. The process can be expressed by the following reaction scheme:

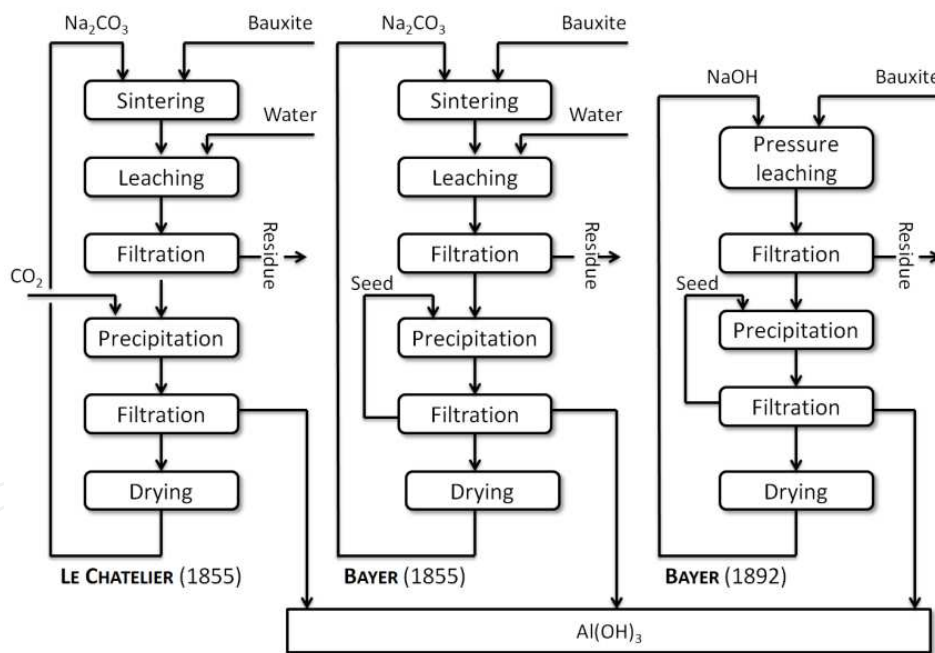
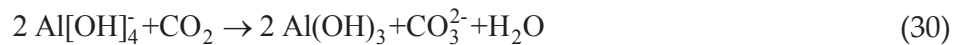


Figure 8. Bayer process of the production of alumina.

The ultrasound [193] and the addition of organics such as methanol [194] and crown ether [195] intensify the nucleation and crystallization of sodium aluminate solution, which has the potential to enhance the throughput of a Bayer process. On the contrary, polyols [196], oleic acid [197] and alditols of hydroxycarboxylic acids [198] inhibit the gibbsite precipitation from seeded sodium aluminate liquors.

1.3. Utilization of red mud

The treatment and utilization of red mud waste are major challenge for the alumina industry. The main environmental risks associated with bauxite residue are related to high pH and alkalinity and minor and trace amounts of heavy metals and radionuclides. Many efforts are being globally made to find suitable applications for red mud so that the alumina industry may end up with no residue [199].

The possible applications of red mud include [199-204]:

- Building/construction materials such as bricks, stabilized blocks, light weight aggregates and low density foamed products.
- In cement industry as cements, special cements, additives to cements, mortars, construction concretes, repairs of roads, pavements, dykes.
- Colouring agents for paint works for ground floors of industrial and other buildings.
- Foamed paper in wood pulp and paper industry.
- Reinforced red mud polymer products, ceramic/refractory products.
- In metallurgical industries, as raw material in iron and steel industry as a sinter aid (binder) for iron ores, flux in steel making, etc.
- Micro-fertilizer and a neutralizer of pesticides in agriculture.
- Extracting rare-earth metals and alumo-ferric coagulants as technical raw materials.
- Special use as inorganic chemicals, adsorbents, etc.

1.4. Methods of production of high purity Al_2O_3

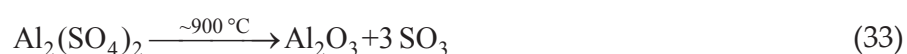
Aluminium oxide of high purity and high specific surface area can be prepared by thermal decomposition of alum ($\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$)¹³. Pure ammonium alum crystal is colorless and transparent and belongs to cubic crystal system. Melting temperature of ammonium alum crystal is 94.5 °C with the phase transition enthalpy of 122.2 kJ mol⁻¹. [205-209]. $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ is widely applied in industries and in water treatment [210,211]. Recently, ammonium alum is used as a promising material for Raman laser converters with a large frequency shift [212], for ferroelectricity [213] and phase transitions for storing energy

¹³ Alums can be described by general formula $\text{M}^+\text{Me}^{3+}(\text{RO}_4)_2 \cdot 12\text{H}_2\text{O}$, where M^+ is monovalent cation such as Na^+ , K^+ , Rb^+ , Cs^+ or NH_4^+ , Me^{3+} is trivalent cation such as Al^{3+} , Fe^{3+} , Cr^{3+} and R is S or Se. Each M^+ and Me^{3+} ion is surrounded by an octahedron of six water molecules. A complex network of H-bonds is one of the main features of alum structures. Alums are classified into α ($\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$), β ($\text{CsAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$), and γ ($\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) modifications depending upon three slightly different arrangements of ions and molecules within the cubic lattice. The different structures are characterized by different orientations of sulfate ions with respect to the trigonal axes of unit cell [208,209].

absorbed by solar collectors [214,215], as the catalyst [216,217] and for rubidium recovery from the processing of zinnwaldite [218].

Ammonium aluminum sulfate (AAISD¹⁴) dodecahydrate undergoes the phase transitions at 58 K and 71 K on cooling and heating, respectively. At room temperature $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ crystals have a cubic structure and belong to the space group with four molecules per unit cell with the lattice parameters $a=12.242 \text{ \AA}$. The structural phase transition mechanism is related to the hydrogen-bond transfer involving the breakage of weak part of the hydrogen bond [208].

The process of alum derived synthesis of alumina often produces nanosized powders consisting of amorphous or transition aluminas (Chapter 4.1). The thermal decomposition of aluminium alum can be described according to the following reaction scheme [219]:



The preparation of submicrometer-grained aluminas requires well-defined pure nanopowders which have many exploitable characteristics, such as low-temperature sinterability, greater chemical reactivity and enhanced plasticity. Therefore, whole range of methods was developed for the preparation of nanopowders with desired properties. These can be roughly divided to [424]:

- **High temperature/ flame/ laser synthesis:** the method usually comprises the injection of suitable gaseous or liquid aluminium-containing precursors (e.g. aluminum tri-sec-butoxide) into the source of intensive heat (flame, laser or plasma), where the precursor decomposes and converts into oxide. In most cases, the transient aluminas are formed. Therefore further high-temperature treatment is necessary in order to obtain $\alpha\text{-Al}_2\text{O}_3$.
- **Chemical method including the sol-gel process:** obviously utilizes the low-and medium-temperature decomposition of inorganic aluminium salts and hydroxides or metal-organic compounds of aluminium. Typical precursors include aluminium nitrate and hydroxides.
- **Mechanically assisted synthesis:** the method is based on high-energy milling of coarser-grained powder. In this case, the minimum particle size is limited to approximately 40 nm.

¹⁴ Abbreviation, another example is CsAlSeD ($\text{CsAl}(\text{SeO}_4) \cdot 12\text{H}_2\text{O}$).

- Other options include the combustion synthesis [220-224], the spray pyrolysis of aerosol of nitrate or other aluminum salts [225-227], the sol-gel process [228,229], the emulsion synthesis [230,231], etc.

2. Adjustment of clinker composition

Strontium aluminate is formed via solid-state reaction of equimolar amount of aluminium oxide with strontium oxide:



With regard to the molar weight ratios of $\text{SrO}/\text{Al}_2\text{O}_3=1.016$ and $\text{SrO}/\text{Fe}_2\text{O}_3=0.65$, the proper amount of SrO should be calculated as follows:

$$\text{SrO} = 1.016 \text{ Al}_2\text{O}_3 + 0.65 \text{ Fe}_2\text{O}_3 \quad (35)$$

The mass ratio of used SrO and the theoretical amount calculated according to Eq.34 should be termed as the “**Saturation Degree**” or “**Strontium saturation factor**” of clinker by strontium oxide (SD_{SrO}):

$$SD_{\text{SrO}} = \frac{100 \text{ SrO}}{1.016 \text{ Al}_2\text{O}_3 + 0.65 \text{ Fe}_2\text{O}_3} \quad [\%] \quad (36)$$

Analogically to ordinary Portland cement, the hydraulic module (M_H) and the alumina module (M_A) of strontium aluminate clinker should be defined:

$$M_H = \frac{\text{SrO}}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3} \quad (37)$$

$$M_A = \frac{\text{Al}_2\text{O}_3}{\text{Fe}_2\text{O}_3} \quad (38)$$

To use the strontium aluminate cements for the production of refractory materials the value of $SD_{\text{SrO}} < 100$ and low content of Fe_2O_3 are required. These compositions ensure that the

first eutectic melt is formed at the temperature of 1760 °C instead of 1505 °C for the cement with $SD_{SrO} > 100$.

The composition of mixture of raw materials is calculated from required composition of clinker according to the following relations:

$$SrCO_3 = 1.425 SrO \quad (39)$$

$$Al(OH)_3 = 0.765 \times Al_2O_3 \quad (40)$$

$$others = 100 - SrCO_3 - Al(OH)_3 \quad (41)$$

3. Calculation of the raw meal composition

The preparation of raw meal using only two components is a simple process. The example could be strontium carbonate with 98.4 % $SrCO_3$ and alumina which does not contain any strontium carbonate. The analysing techniques are described in Chapter 2.4. From Eq.34 it can be read that equimolar mixture of $SrCO_3$ and Al_2O_3 ($x_{Al_2O_3} = 0.5$) should be prepared. That means that $x_{SrCO_3} = 0.5$ and $x_{Al_2O_3} = 1 - x_{SrCO_3} = 0.5$. The molar ratio can be recalculated to the weight ratio as follows¹⁵:

$$w = \frac{x_i M_i}{\sum_{j=1}^k x_j M_j} \quad (42)$$

$$\sum_{i=1}^k w_i = 1 \Rightarrow w_k = 1 - \sum_{i=1}^{k-1} w_i \quad (43)$$

From the relationships introduced above we can calculate:

$$w_{SrCO_3} = \frac{0.5 \cdot 147.6}{0.5 \cdot 147.6 + 0.5 \cdot 102.0} = 0.591 \Rightarrow 59.1\% \quad (44)$$

¹⁵ Please see Eqs.18 and 19 in Chapter 1.

$$w_{Al_2O_3} = 1 - 0,591 \Rightarrow 0.409 \Rightarrow 40.9\% \tag{45}$$

The amount of raw mixture constituent can be then calculated:

SrCO₃ 98.4

59.1

P

Al₂O₃ 0

39.3

P

100×59.1/(59.1+39.3)=60.1%

100×39.3/(59.1+39.3)=39.9%

(46)

The raw meal contains 60.1 % of strontium carbonate and 39.9 % of alumina, i.e. both components are mixed in the weight ratio of 1.5 : 1.

3.1. Calculation of required hydraulic module

The preparation of raw meal of given value of hydraulic module (Eq.37) is demonstrated in this chapter. As an example the raw meal for the strontium aluminate clinker with $M_H=0.98$ will be prepared. There are **two raw materials** with the composition given in Table 2.

Raw material		SrO	Al ₂ O ₃	Fe ₂ O ₃	Z =Al ₂ O ₃ +Fe ₂ O ₃
SrCO ₃	1	98.4	0	0.2	0.2
Calcined bauxite	2	0	98.2	1.6	99.8

Table 2. Composition of two raw materials for the preparation of raw meal.

Hence we have two equations:

$$w_1 + w_2 = 100 \tag{47}$$

$$a_{21}w_1 + a_{22}w_2 = 0 \tag{48}$$

where:

$$a_{2i} = SrO - M_H Z_i \quad (i = 1, 2) \tag{49}$$

From the relationships introduced above we can calculate:

$$a_{21} = 98.4 - 0.98 \cdot 0.2 = 98.2 \tag{50}$$

$$a_{22} = 0 - 0.98 \cdot 99.8 = -97.8 \quad (51)$$

From the substitution of 48 by 50 and 51 the following relationship results:

$$\begin{aligned} w_1 + w_2 &= 100 \\ 98.2 w_1 - 97.8 w_2 &= 0 \\ \hline w_1 &= \frac{100 a_{22}}{a_{22} - a_{11}} = \frac{100 \cdot (-97.8)}{-97.8 - 98.2} = 49.9\% \\ w_2 &= \frac{100 (-a_{21})}{a_{22} - a_{21}} = 100 - w_1 = 50.1\% \end{aligned} \quad (52)$$

Now it is possible to check, if the calculated results are correct:

Raw material	Composition			w_i [%]	Raw meal		
	SrO	Al ₂ O ₃	Fe ₂ O ₃		SrO	Al ₂ O ₃	Fe ₂ O ₃
1	98.4	0	0.2	49.9	48,3	0	0,1
2	0	98.2	1.6	50.1	0	49,2	0,8
Total				100.0	49,1	49,2	0,9
M_H				49,1 / (49.2 + 0,9) = 0.98			

Another case is that the mixture requires the preparation via **mixing of three raw materials**, e.g. we have strontium carbonate, calcined bauxite and corundum. Corundum is necessary to keep the value of hydraulic module (M_H)=0.98 and alumina module (M_A)=57. The composition of raw materials is listed in Table 3.

Raw material		SrO	Al ₂ O ₃	Fe ₂ O ₃	Z = Al ₂ O ₃ + Fe ₂ O ₃
SrCO ₃	1	98.4	0	0.2	0.2
Calcined bauxite	2	0	98.2	1.6	99.8
Corundum	3	0	99.5	0.1	99.6

Table 3. Composition of three raw materials for the preparation of raw meal.

$$w_1 + w_2 + w_3 = 100 \quad (53)$$

$$a_{21}w_1 + a_{22}w_2 + a_{23}w_3 = 0 \quad (54)$$

$$a_{31}w_1 + a_{32}w_2 + a_{33}w_3 = 0 \quad (55)$$

Where:

$$a_{2i} = SrO - M_H Z_i \quad (56)$$

$$a_{3i} = Al_2O_3 - M_A Fe_2O_3 \quad (i = 1, 2, 3) \quad (57)$$

From the relationships introduced above we can calculate:

$$a_{21} = 98.4 - 0.98 \cdot 0.2 = 98.2 \quad (58)$$

$$a_{22} = 0 - 0.98 \cdot 99.8 = -97.8 \quad (59)$$

$$a_{23} = 0 - 0.98 \cdot 99.6 = -97.6 \quad (60)$$

$$a_{31} = 0 - 50 \cdot 0.2 = -11.4 \quad (61)$$

$$a_{32} = 98.2 - 50 \cdot 1.6 = 7.0 \quad (62)$$

$$a_{33} = 99.5 - 50 \cdot 0.1 = 93.8 \quad (63)$$

The substitution of equations 53-55 by Eq.58-63 yields to:

$$\begin{array}{rcl} w_1 + w_2 + w_3 & = & 100 \\ 98.2 w_1 - 97.8 w_2 - 97.6 w_3 & = & 0 \\ -11.4 w_1 + 7.0 w_2 + 93.8 w_3 & = & 0 \end{array} \quad (64)$$

The value of determinant D can be calculated as follows:

$$\begin{aligned} D &= a_{22} a_{33} - a_{32} a_{23} - (a_{21} a_{33} - a_{31} a_{23}) + a_{21} a_{32} - a_{31} a_{22} \\ D &= -9174.0 - 683.3 - (9211.5 - 1112.7) + 687.4 - 1115.0 \\ D &= -17017.1 \end{aligned} \quad (65)$$

The composition of raw meal is then:

$$w_1 = \frac{-100 (a_{22} a_{33} - a_{32} a_{23})}{D} = 49.9\% \quad (66)$$

$$w_2 = \frac{-100 (a_{21} a_{33} - a_{31} a_{23})}{D} = 47.6\% \quad (67)$$

$$w_3 = \frac{100 (a_{21} a_{32} - a_{31} a_{22})}{D} = 2.5\% \quad \text{or} \quad (68)$$

$$w_3 = 100 - (w_1 + w_2) = 2.5\%$$

Now it is possible, as previously, to check, if the calculated results are correct:

Raw material	Composition			w_i [%]	Raw meal		
	SrO	Al ₂ O ₃	Fe ₂ O ₃		SrO	Al ₂ O ₃	Fe ₂ O ₃
1	98.4	0	0.2	49.9	49.10	0	0.10
2	0	98.2	1.6	47.6	0	46.74	0.76
3	0	99.5	0.1	2.5	0	2.50	0
Total				100	49.10	49.24	0.86
M_H				$49.10 / (49.24 + 0.86) = 0.98$			
M_A				$49.24 / 0.86 = 57$			

3.2. Calculation from the saturation degree

The method of calculation of raw meal for the preparation of strontium aluminate clinker with given Saturation Degree (SD_{SrO}) and alumina module (M_A) is described. As an example the mixture with $SD_{SrO}=0.95$ and $M_A=60$ using three raw materials with the composition listed in Table 4 will be prepared.

Raw material		SrO	Al ₂ O ₃	Fe ₂ O ₃
SrCO ₃	1	97.3	0	0.3
Calcined bauxite	2	0	96.5	2.6
Corundum	3	0	99.7	0.1

Table 4. Composition of three raw materials for the preparation of raw meal.

The composition of raw meal results from the solution of the following set of three equations:

$$w_1 + w_2 + w_3 = 100 \quad (69)$$

$$a_{21}w_1 + a_{22}w_2 + a_{23}w_3 = 0 \quad (70)$$

$$a_{31}w_1 + a_{32}w_2 + a_{33}w_3 = 0 \quad (71)$$

where

$$a_{2i} = \text{SrO-SD}_{\text{SrO}} (1.016 \text{ Al}_2\text{O}_3 + 0.65 \text{ Fe}_2\text{O}_3) \quad (72)$$

$$a_{3i} = \text{Al}_2\text{O}_3 - M_A \text{ Fe}_2\text{O}_3 \quad (i = 1, 2, 3) \quad (73)$$

From the relationships introduced above we can calculate:

$$a_{21} = 90.3 - 0.96 (1.016 \cdot 0 + 0.65 \cdot 0.3) = 90.2 \quad (74)$$

$$a_{22} = 0 - 0.96 (1.016 \cdot 96.5 + 0.65 \cdot 2.6) = -95.6 \quad (75)$$

$$a_{23} = 0 - 0.96 (1.016 \cdot 99.7 + 0.65 \cdot 0.1) = -97.2 \quad (76)$$

$$a_{31} = 0 - 60 \cdot 0.3 = -18.0 \quad (77)$$

$$a_{32} = 96.5 - 60 \cdot 2.6 = -59.5 \quad (78)$$

$$a_{33} = 99.7 - 60 \cdot 0.1 = 93.7 \quad (79)$$

The value of determinant D can be calculated as follows:

$$\begin{aligned} D &= a_{22} a_{33} - a_{32} a_{23} - (a_{21} a_{33} - a_{31} a_{23}) + a_{21} a_{32} - a_{31} a_{22} \\ D &= -8960.3 - 5783.9 - (9099.7 - 1749.8) - 5778.4 - 1721.3 \\ D &= -29593.8 \end{aligned} \quad (80)$$

The composition of raw meal is then:

$$w_1 = \frac{-100 (a_{22} a_{33} - a_{32} a_{23})}{D} = 49.8\% \quad (81)$$

$$w_2 = \frac{-100 (a_{21} a_{33} - a_{31} a_{22})}{D} = 24.8\% \quad (82)$$

$$w_3 = \frac{100 (a_{21} a_{32} - a_{31} a_{22})}{D} = 25.3\% \quad \text{or} \quad (83)$$

$$w_3 = 100 - (w_1 + w_2) = 25.3\%$$

Now it is possible, as previously, to check, if the calculated results are correct:

Raw material	Composition			w_i [%]	Raw meal		
	SrO	Al ₂ O ₃	Fe ₂ O ₃		SrO	Al ₂ O ₃	Fe ₂ O ₃
1	97.3	0	0.3	49.8	48.48	0	0,15
2	0	96.5	2.6	24.8	0	23.97	0,65
3	0	99.7	0.1	25.3	0	25,27	0,03
Total				100	48,48	49,23	0,82
M _H				48.48/ (49.23 + 0.82) = 0.97			
M _A				49.23/ 0.82 = 60			

3.3. Calculation with SD_{SrO} , M_A and other parameter

Using four raw materials for the preparation of raw meal where other parameter can be used for calculation. That can be useful for the preparation of cement with exceeding substitution of alumina. For example, the Saturation Degree of clinker by strontium oxide and alumina module can be redefined as follows:

$$SD_{SrO}^* = \frac{100 \text{ SrO}}{1.016 \text{ Al}_2\text{O}_3 + 0.65 \text{ Fe}_2\text{O}_3 + 0.68 \text{ Cr}_2\text{O}_3} \quad [\%] \quad (84)$$

$$M_A^* = \frac{\text{Al}_2\text{O}_3}{\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3} \quad (85)$$

Therefore a new type of module can be applied:

$$M_{Fe}=\frac{Fe_2O_3}{Cr_2O_3} \tag{86}$$

This is the case of raw meal the preparation of strontium aluminate clinker with following parameters $SD_{SrO}^*=0.90$, $M_A^*=58$ and $M_F=10$. The composition of raw materials is listed in Table 5.

Raw material		SrO	Al ₂ O ₃	Fe ₂ O ₃	Cr ₂ O ₃	Y=Fe ₂ O ₃ +Cr ₂ O ₃
SrCO ₃	1	97.3	0	0.3	0	0.3
Calcined bauxite	2	0	96.5	2.6	0	2.6
Corundum	3	0	99.7	0.1	0	0.11
Cr ₂ O ₃	4	0	2.8	1.5	32.6	34.1

Table 5. Composition of four raw materials for the preparation of raw meal.

The composition of raw meal results from the solution of the following set of four equations:

$$w_1 + w_2 + w_3 + w_4 = 100 \tag{87}$$

$$a_{21}w_1 + a_{22}w_2 + a_{23}w_3 + a_{24}w_4 = 0 \tag{88}$$

$$a_{31}w_1 + a_{32}w_2 + a_{33}w_3 + a_{34}w_4 = 0 \tag{89}$$

$$a_{41}w_1 + a_{42}w_2 + a_{43}w_3 + a_{44}w_4 = 0 \tag{90}$$

Where:

$$a_{2i} = SrO-SD_{SrO}^* \left(1.016 \; Al_2O_3+0.65 \; Fe_2O_3+0.68 \; Cr_2O_3 \right) \tag{91}$$

$$a_{3i} = Al_2O_3-M_A^* \left(Fe_2O_3+Cr_2O_3 \right) \tag{92}$$

$$a_{4i} = Fe_2O_3-M_F \; Cr_2O_3 \qquad \left(i=1, 2, 3, 4 \right) \tag{93}$$

From the relationships introduced above we can calculate:

$$a_{21} = 97.3 - 0.90 (1.016 \cdot 0 + 0.65 \cdot 0.3 + 0.68 \cdot 0) = 97.1 \quad (94)$$

$$a_{22} = 0 - 0.90 (1.016 \cdot 96.5 + 0.65 \cdot 2.6 + 0.68 \cdot 0) = -89.8 \quad (95)$$

$$a_{23} = 0 - 0.90 (1.016 \cdot 99.7 + 0.65 \cdot 0.1 + 0.68 \cdot 0) = -91.2 \quad (96)$$

$$a_{24} = 0 - 0.90 (1.016 \cdot 2.8 + 0.65 \cdot 1.5 + 0.68 \cdot 32.6) = -23.4 \quad (97)$$

$$a_{31} = 0 - 58.0 (0.3 + 0) = -17.4 \quad (98)$$

$$a_{32} = 96.5 - 58.0 (2.6 + 0) = -54.3 \quad (99)$$

$$a_{33} = 99.7 - 58.0 (0.1 + 0) = 93.9 \quad (100)$$

$$a_{34} = 2.8 - 58.0 (1.5 + 32.6) = -1975.0 \quad (101)$$

$$a_{41} = 0.3 - 10.0 \cdot 0 = 0.3 \quad (102)$$

$$a_{42} = 2.6 - 10.0 \cdot 0 = 2.6 \quad (103)$$

$$a_{43} = 0.1 - 10.0 \cdot 0 = 0.1 \quad (104)$$

$$a_{44} = 1.5 - 10.0 \cdot 32.6 = -324.5 \quad (105)$$

From the relationships introduced above we can further calculate:

$$w_1 + w_2 + w_3 + w_4 = 100 \quad (106)$$

$$97.1 w_1 - 89.8 w_2 + -91.2 w_3 - 23.4 w_4 = 0 \quad (107)$$

$$-17.4 w_1 - 54.3 w_2 + 93.9 w_3 - 1975.0 w_4 = 0 \quad (108)$$

$$0.3 w_1 + 2.6 w_2 + 0.1 w_3 - 324.5 w_4 = 0 \quad (109)$$

The solution based on the Sauruss law is time consuming without specialized software. Nevertheless, it is possible to use the calculation according to Table 6. This solution is based on the Gauss inversion method. The symbols i and k denote the line and column of matrix for mathematical operation according to given rule, e.g. $2a_1$ is the second line and the first column member of matrix. The solution consists of the following steps:

- i. Inserting the coefficients from the left side of Eqs.106-109 into proper line (1-4) of Table 6. For example the coefficient a_{11} from Eq.106 should be written in the first line and first column; the coefficient a_{32} belongs to the third line and second column, etc.
- ii. The column I contains the sum of members 1-4 for given line.
- iii. The column II contains the coefficients from the right side of Eqs.106-109 for the line from 1 to 4. Other lines refer to the results of mathematical operation defined in the column rule.
- iv. The operation on line 6 ($-2a_1 \bullet 5+2$) means: $-97.13 \bullet 1.00+97.13=0$, where $2a_1$ is the coefficient related to the second line and first column. The operation $1 : 1a_1$ means that all numbers in the first line are divided by given term.
- v. The last four lines of column II provide the solution for the composition of raw meal.

Rule	Matrix					Test: 4		Test:
	i ^k					Σi	i _b	I+II.
		1	2	3	4	I	II	III
i a _k	1	1.00	1.00	1.00	1.00	4.00	100.00	104.00
	2	97.13	-89.76	-91.22	-23.39	-107.25	0.00	-107.25
	3	-17.40	-54.30	93.90	-1975.0	-1952.8	0.00	-1952.8
	4	0.30	2.60	0.10	-324.50	-321.50	0.00	-321.50
1 :1a ₁ XX	5	1.00	1.00	1.00	1.00	4.00	100.00	104.00
-2a ₁ • 5 + 2	6	0.00	-186.89	-188.35	-120.51	-495.75	-9712.45	-10208.2
-3a ₁ • 5 + 3	7	0.00	-36.90	111.30	-1957.6	-1883.2	1740.00	-143.2
-4a ₁ • 5 + 4	8	0.00	2.30	-0.20	-324.80	-322.70	-30.00	-352.7
-5a ₂ • 10 + 5	9	1.00	0.00	-0.01	0.36	-1.35	48.03	49.38

Rule	Matrix					Test: 4		Test:
	i^k					Σi	i_b	I+II.
		1	2	3	4	I	II	III
6 : 6a ₂ XX	10	0.00	1.00	1.01	0.64	2.65	51.97	54.62
-7a ₂ • 10 + 7	11	0.00	0.00	148.49	-1933.8	-1785.32	3657.70	1872.38
-8a ₂ • 10 + 8	12	0.00	0.00	-2.52	-326.28	-328.80	-149.53	-478.33
-9a ₃ • 15 + 9	13	1.00	0.00	0.00	0.25	1.25	48.22	49.48
-10a ₃ • 15 + 10	14	0.00	1.00	0.00	17.77	14.77	27.14	41.91
11 : 11a ₃ XX	15	0.00	0.00	1.00	-13.02	-12.02	24.63	12.61
-12a ₃ • 15 + 12	16	0.00	0.00	0.00	-359.08	-359.08	-87.51	-446.58
-13a ₄ • 20 + 13	17	1.00	0.00	0.00	0.00	1.00	48.16	49.16
-14a ₄ • 20 + 14	18	0.00	1.00	0.00	0.00	1.00	23.79	24.79
-15a ₄ • 20 + 15	19	0.00	0.00	1.00	0.00	1.00	27.81	28.81
16 : 16a ₄ XX	20	0.00	0.00	0.00	0.00	1.00	0.24	1.24

Table 6. Numerical solution for raw meal four raw materials.

Now it is possible, as previously, to check, if the calculated results are correct:

Raw material	Composition				w_i [%]	Raw meal			
	SrO	Al ₂ O ₃	Fe ₂ O ₃	Cr ₂ O ₃		SrO	Al ₂ O ₃	Fe ₂ O ₃	Cr ₂ O ₃
1	97.3	0	0.3	0	48.16	46.86	0	0.14	0
2	0	96.5	2.6	0	23.76	0	22.96	0.62	0
3	0	99.7	0.1	0	27.81	0	27.72	0.03	0
4	0	2.8	1.5	32.6	0.24	0	0.01	0	0.08
Total					100.00	46.86	50.69	0.79	0.08
SD* _{SrO}	46.86/ (1.016•50.69 + 0.65•0.79 + 0.68•0.08) = 0.90								
M _A *	50.69/ (0.79 + 0.08) = 58.0								
M _{Fe}	0.79/ 0.08 = 10.0								

It is also possible to define another kind of module using V₂O₃, Ti₂O₃ or their mixture with Fe₂O₃ and to calculate the raw meal composition by the same way. This calculation certainly requires the redefinition of Saturation Degree of clinker from strontium oxide to applied system.

4. Method of analysis of raw material and clinker

The calculation mentioned above requires the analysis of raw materials to calculate the correction of working mixture composition. Some techniques applicable for the analysis of raw materials or cements are presented in this chapter. Chemical analysis, microscopy, XRD and other methods of examination should be carried out on the same, representative sample of material [7].

4.1. Determination of SrO

The EDTA disodium salt (Ethylenediaminetetraacetic acid disodium salt dehydrate, $\text{Na}_2\text{H}_2\text{Y} \cdot 2\text{H}_2\text{O}$) titration is the most common technique used for the determination of strontium oxide in the strontium carbonate:



with the stability constant of complex:

$$K(\text{SrY}^{2-}) = \frac{[\text{SrY}^{2-}][\text{H}^+]^2}{[\text{Sr}^{2+}][\text{H}_2\text{Y}^{2-}]} = 398.1 \quad (111)$$

$$\log K(\text{SrY}^{2-}) = 8.6 \quad (112)$$

The formation of stable complex during the assessment requires the $\text{pH} \geq 10$ (the same pH range as for Mg^{2+} and Ba^{2+}).

4.2. Determination of SrO in OPC

In compliance with the current ASTM Standard Test Methods for chemical analysis of hydraulic cement (C 114) [241], strontium (usually present in Portland cement as minor constituent), is led to precipitate (Table 1) with calcium (CaC_2O_4) as oxalate (SrC_2O_4 , monoclinic, space group P21/n [242,243]) and next it is subsequently titrated and calculated as CaO, or alternative correction of CaO for SrO is made, if the SrO content is known. Therefore, the development of a new, direct, sensitive and accurate method for the determination of strontium as minor constituent in cement is of utmost importance [244].

Strontium oxalate exists in two different forms [245]:

1. Neutral strontium oxalate hydrate, $\text{SrC}_2\text{O}_4 \cdot x\text{H}_2\text{O}$.
2. Acid salt of strontium oxalate, $\text{SrC}_2\text{O}_4 \cdot y\text{H}_2\text{C}_2\text{O}_4 \cdot x\text{H}_2\text{O}$.

Depending on the concentration of oxalic acid and ammonium oxalate as precipitating agents, both forms can be obtained. At sufficiently low pH, the stoichiometric compound $\text{SrC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ is formed. The morphologies of precipitated particles (bi-pyramids, rods, peanuts, spheres, etc.) depend on the experimental conditions such as pH, temperature, ageing time and concentration of additives [246].

The structure of acidic strontium oxalate is shown in Fig.9(a). Oxalate and hydrogen oxalate anions are present in such a way that each asymmetric unit contains exactly one molecule with the structural formula $\text{Sr}(\text{HC}_2\text{O}_4) \cdot \frac{1}{2}(\text{C}_2\text{O}_4)\text{H}_2\text{O}$ instead of $\text{Sr}(\text{C}_2\text{O}_4) \cdot \frac{1}{2}(\text{H}_2\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$. Similarly to other known strontium oxalates, strontium is eight-fold coordinated by oxygen. In this coordination sphere, both, oxalate and hydrogen oxalate anions act once as bidentate and once as monodentate. Two remaining positions are occupied by H_2O molecules. The SrO_8 polyhedron can be described as distorted bicapped trigonal prism, with $\text{O7} \dots \text{O2} \dots \text{O5} \dots \text{Ow3}$ forming the square face. These polyhedrons are connected to each other only by edge sharing it to form one-dimensional chains along the c-axis [242].

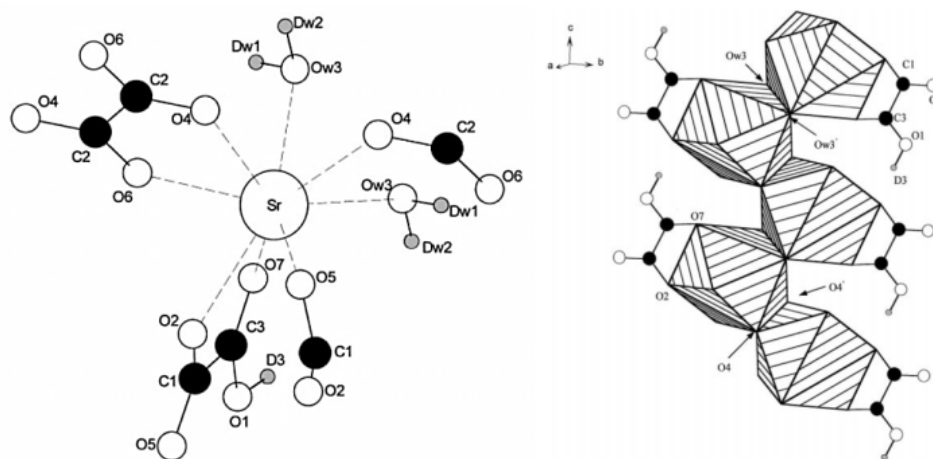


Figure 9. Strontium oxalate: Structure of SrO_8 polyhedron (a) and connection of polyhedrons via shared edge (b) according to [243].

The shared edges are $\text{O4} \dots \text{O4}'$ and $\text{Ow3} \dots \text{Ow3}'$ (Fig.9 (b)), which means that H_2O acts as bridging ligand between two strontium atoms. This is in contrast to all other Sr oxalates, where H_2O is also coordinated to Sr, but without any bridging function. In the ac plane, the polyhedra chains are connected by the $\text{C}_2\text{O}_4^{2-}$ groups, while in the bc plane the connection is made by the HC_2O_4^- groups. In addition, there is the possibility to form intrachain ($\text{Dw2} \dots \text{O5}$ and $\text{D3} \dots \text{O2}$ along the bc plane) as well as interchain ($\text{Dw1} \dots \text{O6}$ along the ac plane) hydrogen bridges, which give the whole network an extra stability. Until now the four types of acid strontium oxalates are known, the type 2 and 4 are conformers (Fig.10) with calculated energy difference of $\sim 6.69 \text{ kJ mol}^{-1}$ [242,243].

Many analytical techniques were suggested for the determination of strontium in the cement matrix [238,247-250], i.e. under conditions including high concentration of calcium in the sample, based on complicated separation techniques of low selectivity. The atomic absorp-

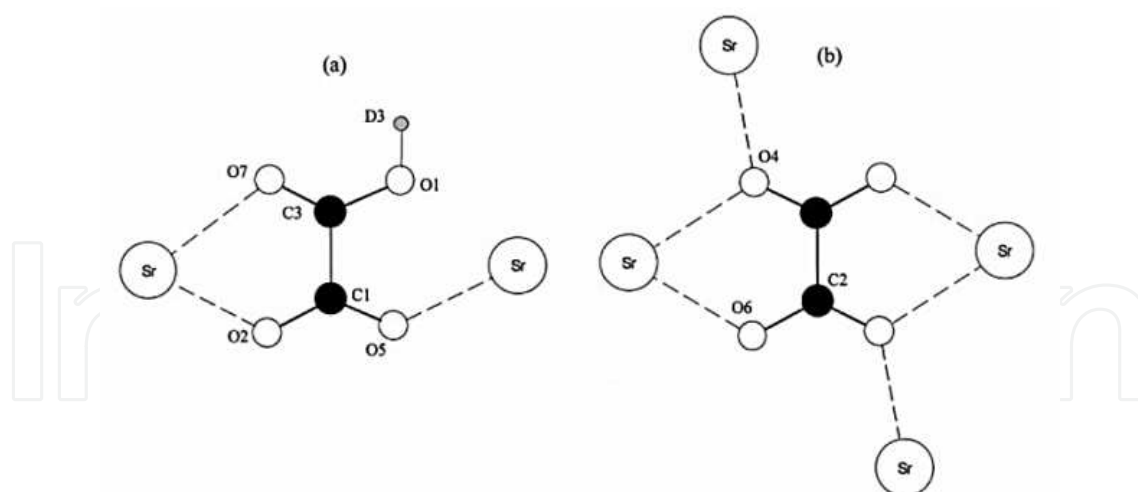


Figure 10. Coordination types of acid strontium oxalate: type 4 (a) and type 2 (b).

tion spectrometric method can be used for the determination of calcium, magnesium and strontium in soils [236] but the assessment requires the removal of the silicon.

Derivative spectrophotometry is analytical technique combining high selectivity [251-255] and sensitivity [244,256-258]. The accuracy of assessment depends on the shape of normal absorption spectra of analyte and interfering substances, as well as on the instrumental parameters and the applied technique of measurement, e.g. peak-to-trough or zero-crossing [259-261]. Salinas et al. [262] developed the derivative spectrophotometric method for resolving binary mixtures when the spectra of components are overlapped. The method uses the first derivation of the spectra. The concentration of other component is then determined from the calibration graph. Later, the method was extended to the resolution of ternary mixtures in combination with zero-crossing method [263].

The determination of strontium and simultaneous determination of strontium oxide, magnesium oxide and calcium oxide content in Portland cement by derivative ratio spectrophotometry uses alizarin Complexone (alizarin-3-methylamine-N, N-diacetic acid, AC) as one of the most common reagents used for the spectrophotometric determination of metal ions. The AC reagent yields five colored acid-base forms in the solutions of pH ~3.2–10.5: H_4L , H_3L^- , H_2L^{2-} , HL^{3-} and L^{4-} , exhibiting the absorption maxima at 270, 335, 423, 525, and 580 nm, respectively. Distinct isosbestic points are observed for the particular acid-base equilibrium. The formation of SrL^{2-} complex with liberation of one proton occurs in pH range from 7 to 10 [262]:



The determination of strontium as SrL^{2-} complex was possible in the presence of Li^+ , Na^+ , K^+ , Cs^+ , Cd^{2+} , Al^{3+} , Fe^{3+} , Mo^{6+} , SO_4^{2-} , SO_3^{2-} , NO_3^- , Cl^- , Br^- , I^- and PO_4^{3-} (20.0 mg); Co^{2+} , Ni^{2+} , Pb^{2+} , Cr^{3+} , Ti^{4+} , $C_2O_4^{2-}$ and CO_3^{2-} (1.0 mg). Investigated ions Ca^{2+} , Mg^{2+} , Mn^{2+} and Zn^{2+} interfered se-

riously, even when present in amounts higher than 0.1 mg. The interference due to Mn and Zn was eliminated by the addition of ammonium hydroxide, and that of Ca and Mg was overcome by using the derivative ratio zero crossing method. Using the proposed method, it is possible to determine Sr, Mg, and Ca simultaneously in mixtures containing 1.5-18 $\mu\text{g}\cdot\text{cm}^{-3}$ of strontium, 0.5-5.0 $\mu\text{g}\cdot\text{cm}^{-3}$ of magnesium and 1.0-8.0 $\mu\text{g}\cdot\text{cm}^{-3}$ of calcium [262].

4.3. Application of strontium isotopes to determine the origin of cements in concrete

In many disciplines of science it is important to be able to determine the source of material or to characterize its transportation history. The chemical composition has been used extensively to determine the source of materials by fingerprinting the chemical composition of the material to be identified and comparing it to the chemical composition of potential sources. This approach has been used extensively for major elements as well as for trace elements [264,265].

Forensic isotope geochemistry relies on subtle differences in isotopic abundance of element to characterize particular material. These different isotopic abundances give rise to unique isotopic composition that will identify the material come from particular region. Many rocks composed of different minerals have distinctive isotopic compositions and their unique composition can be used to fingerprint them. This distinctive rock/mineral composition usually arises from the decay of radiogenic elements e.g., ^{87}Rb to ^{87}Sr ; the transuranic elements to ^{208}Pb , ^{207}Pb , ^{206}Pb , ^{147}Sm to ^{143}Nd [264].

Combined chemical and Sr isotopic analysis may provide the geochemical fingerprints from raw materials, which can be used to identify them in concrete. For successful chemical fingerprinting of cement in concrete, it is important to leach cement without significantly attacking the aggregate, but this can be minimized by using slightly alkaline or neutral EDTA as solvent in preference to weak mineral acids such as HNO_3 . Combined chemical and Sr isotopic analysis of commonly used New Zealand cements showed that they contain characteristic fingerprints, which may be used to identify them in concrete of unknown origin. Although cements have typically $^{87}\text{Sr}/^{86}\text{Sr}$ values similar to their mid-Tertiary limestone source rocks (0.7078 – 0.7085) most are easily distinguishable when their $^{87}\text{Sr}/^{86}\text{Sr}$ values are plotted against Ca/Sr [266].

4.4. Determination of Al_2O_3 and Fe_2O_3

Different forms of alumina may be identified by x-ray diffraction analysis [91]. Classical, wet analysis gives inaccurate results for Al_2O_3 unless the effects of P_2O_5 and TiO_2 are not taken into account [7].

5. Method for analysis of SrAC cement

The standard test methods for the chemical analysis of hydraulic cement are specified by ASTM C 114-13. The chemical analysis of hydraulic cement is specified by ASTM C 114-88

standard. The mineralogy of cement cannot be determined from the chemical composition because the thermodynamic equilibrium usually is not reached during the production process. The phase (mineralogical) composition of strontium aluminate cement can be in principle determined by the same methods as for aluminous cements:

1. Selective dissolution [269];
2. Electron Microscopy [7,269];
3. Reflected Light Microscopy [7,269];
4. Quantitative X-Ray Diffraction Analysis (QXDA) [7,267-270,599],

Due to recent developments in cement clinker engineering, the optimization of chemical substitutions in the main clinker phases offers a promising approach to improve both reactivity and grindability of clinkers. Thus, the monitoring of chemistry of phases may become a part of the quality control at cement plants, along with usual measurements of the abundance of mineralogical phases [270].

6. Determination of water to cement ratio

The chemical reactions which take place after mixing cement with water are generally more complex than simple conversion of anhydrous compounds into the corresponding hydrates. The mixtures of cement with water, where the hydration reactions, setting and hardening take place are termed as pastes [271], while the hardened material can be termed as cement stone or hardened cement stone. The water to cement ratio (w/c) refers to the proportion by mass that is related to water and cement used for the preparation of cement paste [12,271].

The value water-to-cement (w/c) ratio is one of the most fundamental parameters in concrete mixture proportioning. The w/c ratio has a significant influence on most properties of hardened concrete, in particular on strength and durability due to its relationship with the amount of residual space i.e. capillary porosity, in the cement stone. Since the w/c ratio is an indication of quality of concrete mix, the situations often arise in which it is desirable to determine the original w/c ratio of particular concrete some time after it has hardened. This often happens when the disputes suspecting the noncompliance with the mix specification arise. The determination of the w/c ratio is also important for the quality control during the concrete production and for general quality assurance purposes [273-277].

Unfortunately, once concrete has set, it is very difficult to ascertain the exact amounts of cement and water which were originally added during batching. At any moment after setting, the hardened cement stone can be considered to consist of four main phases [273]:

1. Rest of unreacted cement;
2. Crystalline and semi-crystalline hydration products including their intrinsic gel pores;
3. Capillary pores;

4. Air voids.

The solid hydration products occupy a greater volume than the volume of reacted cement (Fig.11), but slightly smaller volume than the sum of volumes of cement and water due to chemical shrinkage [273,278]. Chemical shrinkage associated with hydration of OPC and AC is about 5 and 10 – 12 ml per 100 g of cement, respectively [12].

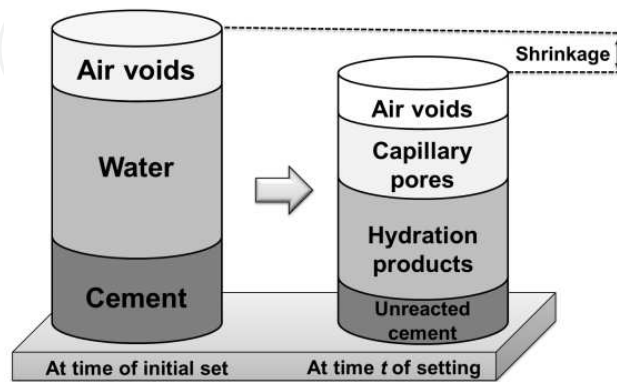


Figure 11. Proportion of main phases in hardened cement stone [273].

The methodology for the estimation of initial cement content, water content and water/cement ratio of hardened cement-based materials by electron microscopy was developed by Wong and Buenfeld [273] and Sahu et al. [275]. The acoustic-ultrasonic approach for non-destructive determination of w/c ratio was described by Philippidis and Aggelis [274]. Betcher et al. [277] published the method using 2.45 GHz microwave radiation which can be conveniently and accurately used for the on-site determination of the water-to-cement (w/c) ratio in a batch of fresh rapid-setting concrete.

7. Grinding

Grinding occurs at the beginning and at the end of cement making process [279]. In recent years, the matrix model and the kinetic model, which were suggested by investigators, are used in laboratories and industrial areas. The kinetic model, which is an alternative approach, considers the combination as a continuous process in which the rate of breakage of particle size is proportional to the mass of particles of that size. The analysis of size reduction in tumbling ball mills using the concepts of specific rate of breakage and primary daughter fragment distribution has received considerable attention in the last years [280,320].

To optimize the cement grinding, the standard Bond grinding calculations [281] can be used as well as the modeling and simulation techniques based on the population balance model (PBM) [284,285]. The mill power draw prediction can be carried out using the Morrell power model for tumbling mills [279,282].

The Bonds equation describes the specific power required to reduce the feed from specified feed F_{80} to the product with specified P_{80} [279,281]:

$$W_m = W_i \left(\frac{10}{\sqrt{P_{80}}} - \frac{10}{\sqrt{F_{80}}} \right) \quad (114)$$

where W_m is the mill specific motor output power ($\text{kWh} \cdot \text{t}^{-1}$), W_i is the Bond ball mill work index ($\text{kWh} \cdot \text{t}^{-1}$), P_{80} is the sieve size passing 80 % of the mill product (μm), F_{80} is the sieve size passing 80 % of the mill feed (μm). It was found in the crushing area that there are significant differences between the real plant data and the Bond calculations and therefore the empirical corrections were introduced. The following modified Bond equation was proposed for crushing [283]:

$$W_c = \frac{A}{\sqrt{P_c}} W_i \left(\frac{10}{\sqrt{P_c}} - \frac{10}{\sqrt{F_c}} \right) \quad (115)$$

where W_c is the energy consumed for crushing the clinker (kWh t^{-1}), W_i is the Bond ball mill work index (kWh t^{-1}), P_c is the sieve size passing 80% of clinker after crushing (μm), F_c is the sieve size passing 80% of clinker before crushing (μm) and A is the empirical coefficient, which depends on clinker and crusher properties.

Based on the above considerations for crushing and grinding, the energy consumption for the clinker pre-crushing and ball milling can be estimated using the following Bond based model:

$$W = W_c + W_m \quad (116)$$

Since the pre-crushing product size P_c is equal to the mill feed size F_{80} then [279]:

$$W = \frac{A}{\sqrt{F_{80}}} W_i \left(\frac{10}{\sqrt{P_{80}}} - \frac{10}{\sqrt{F_c}} \right) + 1.3 \left(\frac{2.44}{D} \right)^{0.2} \left\{ \left[R_r + (W_i - 7) \left(\frac{F_{80} - F_0}{F_0} \right) \right] / R_r \right\} \frac{P_{80} + 10.3}{1.145 P_{80}} W_i \left(\frac{10}{\sqrt{P_{80}}} - \frac{10}{\sqrt{F_{80}}} \right) \quad (117)$$

where D is the interior mill diameter and $R_r = F_{80}/P_{80}$.

The basis of the population balance model for modeling the two-compartment ball mill is the perfect mixing ball mill model. This model considers a ball mill or a section of it as a perfectly stirring tank. Then the process can be described in the terms of transport through

the mill and breakage within the mill. Because the mill or section of it is perfectly mixing a discharge rate, d_i , for each size fraction is an important variable for defining the product [279,284,285]:

$$p_i = d_i s_i \quad (118)$$

Steady state operation conditions can be described by the following relation:

$$f_i - r_i s_i + \sum_{j=1}^i a_{ij} r_j s_j - d_i s_i = 0 \quad (119)$$

The substitution of s_i by p_i/d_i leads to the equation:

$$f_i - r_i \frac{p_i}{d_i} + \sum_{j=1}^i a_{ij} r_j \frac{p_j}{d_j} - p_i = 0 \quad (120)$$

where f_i is the feed rate of size fraction [$\text{t} \cdot \text{h}^{-1}$], p_i is the product flow of size fraction [$\text{t} \cdot \text{h}^{-1}$], a_{ij} is the mass fraction of particle of size that appears at size i after breakage, r_i is the breakage rate of particle size i [h^{-1}], s_i is the amount of size i particles inside the mill [t], d_i is the discharge rate of particle size i [h^{-1}]. If the breakage distribution function is known, the calibration of the model to a ball mill involves the calculation of r/d values using the feed and product size distribution obtained under known operating conditions. Where the size distribution of the mill content is available, the breakage and discharge rates can be calculated separately.

The model consists of two important parameters, the breakage function (a_{ij}) that describes the material characteristics and the breakage/discharge rate function (r_i/d_i) which defines the machine characteristics and can be calculated when the feed and product size distributions are known and the breakage function is available. The air classifier controls the final product quality. Therefore, the air classifier has a crucial role in the circuit and a strong attention is paid regarding the design and operation of the air classifier. The classification action is modeled using the efficiency curve approach. The effect of the classifier design and of operational parameters on the efficiency is complicated and the works proceed to improve the current models [279].

7.1. Consumption of grinding media

The consumption of steel grinding media plays an important role in the economics of grinding and as a consequence also in the overall processing of a large variety of ores. The cost associated with grinding media is chiefly determined by two factors; the price and the wear performance of the grinding media. The mass losses of grinding media can be

attributed to three basic mechanisms; the abrasion, the impact and the corrosion. These mechanisms can be simultaneously active in given grinding environment, leading to complex interactions [286].

7.2. Grinding aids

The action of grinding media within the rotating mill not only crushes the existing clinker particles, but also sharply compresses them, which in fact leads to the formation of electrostatic surface charges of opposed polarity. The cement particles agglomerate as a result of the forces of attraction acting on them. Consequently, the cement particle agglomeration reduces the efficiency of mill. The extent of agglomeration depends on [287]:

- The specific characteristics of materials to be ground;
- The operating parameters of mill;
- The efficiency and distribution of grinding media;
- The fineness of cement particles;
- The internal operating conditions of mill (humidity, temperature, ventilation, condition of armor plating, etc.).

Additives, such as water, organic liquids and some inorganic electrolytes are used to reduce the surface free energy of the material being ground with a view to improve the grinding efficiency.

In the grinding process, a variety of grinding aids are used. There are aliphatic amines such as triethylenetetramine (TETA), tetraethylenepentamine (TEPA) and aminealcohols such as diethanolamine (DEA), triethanolamine (TEA) and triisopropanolamine (TIPA). Glycol compounds are represented such as ethyleneglycol (EG), diethyleneglycol (DEG). In addition, there are more complex compounds such as aminoethylethanolamine (AEEA) and hydroxyethyl diethylenetriamine (HEDETA). Phenol and phenol-derivates are also used as grinding aids, as well as other compounds, such as amine acetate, higher polyamines and their hydroxyethyl derivatives [287,322].

7.3. Grinding kinetics

Assuming that a grinding mill is equivalent to a chemical reactor with a first-order phenomenological rate of reaction kinetics [288], the rate of decrease in particle size during the batch grinding of brittle material in ball mill can be described by the first-order equation. The breakage rate of such material was expressed in literature as [289]:

$$w_{i,t} = w_{i,0} \exp(-S_i t) \quad (121)$$

where S_i is the specific rate of breakage of feed size i and $w_{i,t}$ is the mass fraction of total charge. For single component ($i=1$) Eq.121 can be rewritten as:

$$\log \frac{w_{1,t}}{w_{1,0}} = -\frac{S_{1,t}}{2.3} \quad (122)$$

The value S_1 for different particle sizes can be estimated by performing the same experiment with uniform-sized material. Different values of S_1 versus the size can then be plotted on *log-log* plot to give a straight line if all the sizes follow the first-order law of grinding kinetics.

The primary breakage distribution ($B_{i,j}$) is also defined in an empirical form in literature as [280,290,319,320]:

$$B_{i,j} = \varphi_i \left(\frac{x_{i-1}}{x_j} \right)^\gamma + (1 - \varphi_j) \left(\frac{x_{i-1}}{x_j} \right)^b ; n \geq i \geq j \quad (123)$$

where $B_{i,j}$ is the mass fraction of primary breakage products, x_i is the largest size, and the parameters φ , γ and β define the size distribution of the material being ground. When plotting the size versus $B_{i,j}$ on log paper, the slope of the lower part of the curve gives the value of γ , the slope of the upper part of the curve gives the value of β , and φ is the intercept [319].

8. Granulation

The spheroidal aggregate of particles is called a granule, ball, pellet, or an agglomerate. The nucleation, compaction, size enlargement, and spheroidization of pellets take place in the course of balling and granulation and related agglomeration processes [291]. The granulation converts fine powder and/or sprayable liquids (e.g. suspensions, solutions or melts) into granular solid products with more desirable physical and/or chemical properties than the original feed material. This size enlargement technique constitutes a key process in many industries such as the pharmaceutical, food, ore processing and fertilizers ones. Particularly, the granulation process has clear advantages regarding the storage, handling and transportation of the final product [292,293].

The new king of agglomeration technology is binder-less granulation, where the original cohesiveness of powder material is utilized to arrange them into granules. The strength of product granules can be much weaker. However, if the product granules are just an intermediate product in a larger process, such weakness has significant advantages. In many material-forming processes, the boundary between granules remains even after shaping due to unnecessary strength of granules. With weaker granules, the density of green bodies produced by the application of the same pressure as for conventional granules can be much higher. In many cases, the binder removal cannot be done completely leaving possible defects caused by carbonaceous pyrolysis residues. Weaker granules can also be advantageous in pharmaceutical processes depending on the purpose of granulation [294].

Using large pellets for the processing of strontium aluminate clinker (Fig.31 in Chapter 4.5) may change the behaviour during thermal treatment as well as some properties of the product due to increasing influence of partial pressure of carbon dioxide on the thermal decomposition of strontium carbonate. The material forming the diffusion barrier as the reaction zone is shifted from the surface into the deeper zones of pellet. Increasing partial pressure of carbon dioxide slows down the rate of thermal decomposition of strontium carbonate and increases the temperature required for the thermal decomposition (please see the discussion in Chapter 4.2) and temporary lack of SrO in the reaction zone. Therefore, the influence of large pellets on prepared strontium aluminate clinker is similar to the usage of mixture with lower saturation degree (discussed in Chapter 4).