Effect of Various Factors on Particle Size Distribution of Tricalcium Aluminate

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Abstract

For the production of high-quality smelter grade alumina, security filtration is used, i.e. fine purification of green liquor from suspended particles of red mud. Nowadays specially synthesised tricalcium aluminate (TCA) is commonly used as a filter media. This material is resistant in contact with hot alkaline aluminate liquor, low-cost in production and waste TCA can be recycled in Bayer cycle as a source of lime and alumina. There are a number of requirements for TCA, e.g.: low content of fine fraction (below 1.5 – 2 µm); average particle size should be at least 8.5 – 10 µm (preferably 15 – 20 µm); particles should have isometric morphology; phase composition should be thermodynamically stable under the given conditions. Filter beds having an insignificant thickness of TCA (2.5 – 5 mm) should provide: high purification with minimum hydrodynamic resistance; high specific throughput of filtrate; minimum contamination of green liquor with calcium oxide; clog-free pores of filter cloth; ease to wash off from filter cloth when replacing the used filter bed with a new one, etc. Despite the similarities in Bayer technology, TCA synthesised for filtration at different plants can have significant differences. This paper analyses various factors affecting TCA characteristics, including the use of seed, CaO/Al_2O_3 ratio, concentration and composition of alkaline aluminate liquor and impurities in liquor, residence time, etc. Dependencies obtained in the investigation provide a more reliable control of TCA synthesis.

Keywords: Tricalcium aluminate or TCA, calcium hydrocarboaluminate or CHCA.

1. Introduction

Currently, a tendency prevails in the world to use as a filter bed specially synthesized tricalcium aluminate (TCA), which can be subsequently recycled as Ca-source in bauxite digestion or disposed as a low-hazard class waste in the mud disposal area.

TCA has a number of advantages: it is resistant in contact with hot alkaline aluminate liquor, low-cost in production, and waste TCA can be recycled in Bayer cycle, which reduces specific lime consumption and secondary losses of alumina. There are a number of requirements for TCA as a filter bed, including:

- low content of fine fraction (below 2–3 µm) to prevent passing through pores of filter cloth and contamination of CaO hydrate product, and clogging filter cloth pores;
- average particle size should be at least 8.5–10 µm (preferably 15–20 µm), to ensure minimum hydraulic resistance and maximum specific filtrate removal from the surface;
- particle shape of TCA should be isometric, since flattened particles cause increased hydraulic resistance;

- phase composition should be thermodynamically stable under filtration conditions, i.e. transformation processes of various forms of hydrocarboaluminates into hydrogarnet, and hexagonal TCA into cubic calcium hydroaluminate (C_3AH_6) should be completed.

TCA synthesized for security filtration at Ural Aluminium Smelter (hereinafter UAZ), differs from TCA synthesized at other plants. The paper analyses factors affecting particle size distribution of TCA produced at UAZ including the use of seed, CaO/Al_2O_3 ratio, concentration and composition of alkaline aluminate liquor, the presence of impurities, and reaction residence time. The dependencies obtained in this investigation enables the determination of the effect of a number of factors on variation in TCA particle size distribution and improved control of the synthesis process.

2. Factors Affecting Properties of TCA as a Material for Filter Bed Formation

The following factors affect chemical and phase composition, morphology and particle size of TCA [1–19]:

- temperature, time and other conditions of lime burning [1];
- composition of burnt lime including the amount of magnesium compounds [1];
- composition of liquid phase used to prepare lime milk $Ca(OH)_2$. It is shown in [2] that larger and isometric $Ca(OH)_2$ crystals and aggregates are formed when lime is slaked with red mud pond water having low alkali content, as compared to the use of spent or green liquor. It has a positive impact on particle size distribution and properties of synthesized TCA;
- the form of Ca-containing compound used for synthesis, for example, CaO, air-slaked lime $Ca(OH)_2$, lime milk, calcium aluminates of various composition, etc.;
- ways of aluminium compound feeding, including sodium aluminate in liquor, gibbsite, calcium aluminates of various composition, etc.;
- TCA synthesis temperature, since it has a limited region of existence;
- period of synthesis, which affects the completeness of phase transformation processes;
- initial molar ratio $CaO:Al_2O_3$ in liquor used for TCA synthesis [3 and 4]. For example, it is recommended in [3] to carry out synthesis at molar (~ weight) ratio $CaO:Al_2O_3$ not exceeding 3. The ratio above 4 leads to increase in filter bed resistance;
- the rate of lime milk introduction into alkaline aluminate liquor during synthesis; since time-expanded dosage is preferable;
- Al_2O_3 and Na_2O total concentrations in liquor, with respect to free caustic alkali;
- availability in liquor of Na_2CO_3 and other inorganic impurities Na_2SO_4, NaCl and their concentrations;
- availability of potassium alkali in liquor [5];
- availability or addition of organic impurities to control size of crystal, in particular to reduce the content of fines ≤ 1.5–2 µm;
- addition of surfactants, for example, sugars [6];
- presence and amount of TCA seed during synthesis;
- addition of special flocculants that, due to flocculation on the surface or inside the filter bed, allows to reduce penetration of fine red mud particles into pores of filter cloth and their clogging, and increases significantly average filtration capacity [2]. Flocculant also allows the thickness of the TCA layer to be reduced.

As one can see, many factors affect the properties of TCA. Most of these factors and their impact on TCA composition are well studied and described in literature. It should be noted that, as a rule, process engineers of alumina refineries are deprived of an opportunity to control the majority of the above factors affecting TCA formation. For example, quality of purchased lime, sodium carbonate and other impurities content in the liquor used for synthesis, etc.

2.1. Temperature Range of TCA Existence, Impact of Impurities and Synthesis Temperature

The temperature range for TCA synthesis is rather narrow and that is due to:

- fields of its thermodynamic stability;
- impact of impurities;
- economic feasibility, etc.

In an alkali-free system **"$CaO-Al_2O_3-H_2O$"** TCA is thermodynamically stable in the temperature range of 20–215 °C [7 and 8].

In the absence of carbonates in the alkaline system **"$CaO-Na_2O-Al_2O_3-H_2O$"** containing sodium as caustic alkali NaOH (for example, for liquors of sodium carbonate-free alkaline sinter digestion), TCA is stable in the temperature range of 100–225 °C [9].

In alkaline system **"$CaO-Na_2O-Al_2O_3-CO_2-H_2O$"** in presence of soda (Na_2CO_3) in liquor, the TCA existence field is substantially modified [10]. At a temperature of up to 90 °C, the calcite ($CaCO_3$) existence field almost completely blocks formation of TCA. Therefore, formation of TCA does not proceed until the completion of reaction of CO_2 removal from the liquor in a form of calcium carbonate. This is the reason for conditions of TCA synthesis recommended by practically all researchers: temperature 96–98 °C and alkaline aluminate liquor concentration by $Na_2O_{caust.}$ at least 120 g/dm^3. Raising the temperature of synthesis above 100 °C is not advisable for economic reasons since it leads to increases in heat consumption.

Under conditions pertinent to the actual process, TCA synthesis in system **"$CaO-Na_2O-Al_2O_3-CO_2-H_2O$"** proceeds under non-equilibrium conditions, with formation of intermediate, thermodynamically unstable phases in the initial period at a temperature above +60–70 °C [11 and 12]. These phases are:

- calcium hydrocarboaluminate $3CaO \times Al_2O_3 \times CaCO_3 \times 11H_2O$ (further CHCA) (in literature referred to as hemicarbonate $[Ca_2Al(OH)_6]_2 \times 0{,}5CO_3 \times nH_2O$);
- calcium hydrocarboaluminate $2CaO \times Al_2O_3 \times 2CaCO_3 \times nH_2O$ (in literature referred to as monocarbonate $[Ca_2Al(OH)_6]_2 \times CO_3 \times nH_2O$).

Due to thermodynamic instability, calcium hydrocarboaluminates decomposed into fine calcite and relatively large TCA grains and aggregates at temperature above 90 °C within ~ 4 hours [4 and 5]. Most researchers believe that it is this multistage process that is largely responsible for formation of a large amount of fine particles in TCA synthesis from Bayer production liquors at alumina refineries.

It is shown in [6] that initially a mixture is formed consisting of hexagonal tricalcium aluminate and calcium hydrocarboaluminate of type $C_4ACO_2H_{11}/C_4AH_{13}$. These two compounds consist of $Ca_2Al(OH)_6^+$ layers with incorporation of various anions (usually CO_3^{2-}, OH^-) between the layers. In addition, between these layers, oxalate ions, $C_2O_4^{2-}$, [13] can also be incorporated. These two compounds are actually formed at the beginning of the process, when $Ca(OH)_2$ or CaO is added to green liquor at a low temperature. They decompose rapidly enough into TCA when the temperature of the process exceeds 50–60 °C. The rate of the stepwise transformation reaction is determined by the temperature [14].

Transformation of CHCA into TCA, in addition to raising the temperature above 60 °C, is also promoted by excess of caustic alkali, which is formed as a result of breakdown of sodium aluminate when alumina is bound to hydrocalumites, and as a result of soda causticization [6]:

$$C_4ACO_2H_{11} + 2NaOH \rightarrow C_3AH_6 + Ca(OH)_2 + Na_2CO_3 + 5H_2O \quad (1)$$

In [11] it is shown that TCA crystals have a form of octahedra, that is characteristic of calcium garnets and hydrogarnets having cubic syngony. CHCA is separated in a form of platelets, which is a factor deteriorating the so-called filtrability index.

In [12], based on a large amount of experimental data including electron microscopy of intermediate products, a scheme of TCA formation was proposed. The evolution of the resulting reaction products is as follows:

- immediately after the mixing of lime milk with alkaline aluminate liquor, rapid dissolution of $Ca(OH)_2$ occurs, leading to local supersaturation and formation of fine particles of CHCA (or TCA) in a form of flat discs and needles within the first 30 seconds;
- most of $Ca(OH)_2$ passes into CHCA (TCA) within the first 10 minutes of the reaction. The formed CHCA particles are aggregated in a form of rosettes;
- mass emergence of rosette-like aggregates occurs from 10 to 20 minutes;
- after 20 minutes, the rosette-like aggregates begin to transform into spherical particles due to their partial local re-dissolution and crystallization of TCA with minimal free surface energy;
- then within 2 hours a tendency is observed towards agglomeration of spherical TCA particles.

It is demonstrated in [12] that the optimal residence time of TCA particle maturation in an intermittent synthesis process is 2 hours. Vigorous mixing also has an impact on production of particles uniform in composition with a minimum amount of coarse and fine particles.

Calculation shows that when liquor containing 25 g/dm^3 of CO_2 used for synthesis interacts with $Ca(OH)_2$, more than 320 g (s)/dm^3 of hydrocarboaluminate ($3CaO \times Al_2O_3 \times CaCO_3 \times 11H_2O$) is formed. The whole amount of calcium, added for synthesis, is immediately bound to CHCA. This is confirmed by the rosette-like shape of crystals. After 20 minutes, transformation of the thermodynamically unstable (at temperature > 60 C) CHCA into TCA, which is confirmed by the change in the shape from disks to isometric (rounded) octahedra. Calcite, precipitated in the course of the transformation is stable under the given conditions and precipitates as fine particles, which leads to the loss of calcium. It is considered that one of the ways to reduce specific consumption of lime for TCA synthesis is the use of liquors with a minimum amount of soda (Na_2CO_3).

Summing up the above data, for the synthesis of TCA crystals that ensure good filtration, it is important to provide:

- synthesis temperature above calcium hydrocarboaluminates range of existence, i.e. ≥ 95–96 °C;
- use liquor with minimum amount of sodium carbonate;
- liquor concentration by Na_2O_{caust} at least 120 g/dm^3;
- holding time sufficient to complete transformation of CHCA into TCA, i.e. more than 2–3 hours. Otherwise, the transformation process will be completed after formation of the layer over the filter cloth, which leads to "tanning" (loss of elasticity) of the cloth and clogging the pores with growing crystals.

It was previously believed that the region of existence of the cubic calcium hydroaluminate $3CaO \times Al_2O_3 \times 6H_2O$ (hereinafter C_3AH_6) is limited by concentration of NaOH [6] and temperature, since above 225–250 °C the following reactions occur:

$$C_3AH_6 + 2NaOH \leftrightarrow 3Ca(OH)_2 + 2NaAl(OH)_4 \tag{2}$$

$$C_3AH_6 + 3Na_2CO_3 \leftrightarrow 3CaCO_3 + 2NaAl(OH)_4 + 4NaOH \tag{3}$$

In actual production, these reactions are of no practical importance, since as the temperature rises, the structure of TCA is stabilized by silica contained in it, and tricalcium hydroaluminate is converted into aluminium-calcium hydrogarnet in the following isomorphic series:

TCA		katoite		hibschite		almandine
$Ca_3Al_2(OH)_{12}$	→	$Ca_3Al_2(SiO_4)_1(OH)_8$	→	$Ca_3Al_2(SiO_4)_2(OH)_4$	→	$Ca_3Al_2(SiO_4)_3$

In the course of structural rearrangement of CHCA into TCA, inclusion of SiO_2 from the liquor into the TCA structure takes place [15]. Isomorphic substitution of hydroxyl groups by silica is one of the hidden reserves of security filtration and is perhaps one of factors that reduce the effect of deviations from optimal synthesis conditions.

2.2. The Impact of Potassium Alkali

According to the data of [5], the presence of potassium alkali in liquor leads to a substantial size degradation of TCA grains from ≥10 µm to about 2–3 µm. In this case, potassium alkali contributes to the formation of a significant amount of 8- and 12-hydrate hydroaluminates in the form of rods in aggregation with 6-hydrate cubic TCA. Perhaps, a relatively high potassium content in UAZ liquors (up to 40 g/dm^3 in terms of K_2O) is one of the factors causing synthesis of fine TCA. Within the scope of this investigation model experiments were conducted to determine the significance of potassium impact on TCA synthesis for UAZ conditions.

2.3. The Impact of Sulphates

When synthesizing TCA from highly diluted liquors containing SO_4^{2-}ions, with an initial temperature of about 85 °C formation of: monosulphoaluminate, ettringite (calcium hydrosulphoaluminate having formula: $Ca_6Al_2(SO_4)_3(OH)_{12} \times 26H_2O$) or gypsum is possible. UAZ liquors contain a significant amount of sulphur of various valence (sulphide and polysulphides, thiosulphate, sulphite, sodium sulphate) formed from elemental sulphur. Gaseous sulphur is added to bind zinc, (which comes with bauxite from the Mid-Timan Bauxite Mine (STBR)) to form insoluble ZnS. Under UAZ conditions, sulphur compounds can affect synthesis only at the beginning of the process. Subsequently, the liquid phase rather quickly reaches an alumina to caustic molar ratio of 20 units and higher. At high Na_2O concentration in liquor and pH>14, gypsum is not formed, since it is thermodynamically unstable. This is proved by chemical analysis of TCA synthesized in sulphur-containing liquors, in which chemical analysis shows low content of total sulphur.

2.4. Initial Composition of Lime

In investigation performed for Sosnovogorsk Alumina Refinery, as applied to magnesian limestones mined in Komi Republic, it was demonstrated that increased magnesium content in lime practically does not affect the particle size of produced TCA [1].

2.5. $CaO:Al_2O_3$ Molar Ratio in Liquor and Liquor Concentration

The Molar $CaO:Al_2O_3$ ratio at the beginning of the synthesis process should meet the criterion of alumina sufficiency for completion of TCA synthesis process, since otherwise there remains unreacted lime that is "encapsulated" in the shell of tricalcium aluminate [4].

Usually for synthesis, alkaline aluminate liquors are used with α_{caust} of 1.5 to 3. Referred here α_{caust} is molar ratio of caustic soda and alumina (see the equation 4).

$$\alpha_{caust} = 1.645\ Na_2O / Al_2O_3 \tag{4}$$

In the course of TCA synthesis, the liquor α_{caust} rises to 20–30 units. This is caused both by binding of Al_2O_3 in TCA, and by soda causticization.

A number of researchers recommend to batch calcium substantially below the stoichiometric amount of 3, e.g., dosage to achieve molar ratio $CaO:Al_2O_3 \leq 1$. After completion of synthesis, dissolved Al_2O_3 should remain in liquor in a sufficient amount. This approach is inconsistent with the data of the investigation carried out in 2006 for UAZ by Institute of Solid State Chemistry, Ural Branch of Russian Academy of Sciences and Research & Development Company "MASHPROM" JSC (Yekaterinburg). It is demonstrated that the increase in dosage of CaO/Al_2O_3 to 1.6 has a positive effect on particle size distribution of produced material [4]. Therefore, it was decided to check up in the laboratory, the effect of changing CaO/Al_2O_3 ratio within a wide range.

A number of researchers recommend carrying out TCA synthesis in liquor diluted with respect to alkali and alumina, e.g., in spent liquor or dilution water. When planning the physical modelling matrix in the laboratory, it was decided to test the effect of changing alumina concentration in liquor fed for synthesis within a wide range.

2.6. The Rate of Lime Milk Feeding

It has been shown that a minimum rate of calcium dosage during synthesis or its feeding in several stages has a positive impact on the rate of TCA crystal growth [6].

2.7. The Impact of Organic Impurities and Surface-Active Additives on Properties of Synthesised TCA

It is known that a number of organic compounds contained in Bayer liquors affect solubility of $Ca(OH)_2$ and, accordingly, formation of TCA crystals [16].

2.8. Sugars

It has been demonstrated that addition of sugar or sucrose allows one to obtain TCA having a round-spherical shape and of larger size [17].

2.9. Oxalates and Coloured Organics

It is known that the oxalate ion is incorporated into the layers of hexagonal tricalcium aluminate and calcium hydrocarboaluminate of type $C_4ACO_2H_{11}$ / C_4AH_{13} [13]. Furthermore, coloured organics contained in Bayer liquors are sorbed on the surface of these hydrocalumites, which significantly delays their structural rearrangement into TCA. It has been shown that sorption of organic impurities between the $Ca_2Al(OH)_6^+$ layers present in C_2AH_8 or C_4AH_{13} can significantly delay their conversion to TCA [18 and 19]. For example, glucose inhibits transition of C_2AH_8 or C_4AH_{13} at 70 °C and completely stops structural rearrangement. Without addition of glucose, structural rearrangement of these compounds is quickly completed.

2.10. Solubility of Calcium Compounds

In [16], the solubility of various calcium compounds in Bayer liquors was studied and the effect on solubility of temperature, soda concentration, caustic and organic impurities was investigated. Solubility in water of Ca-containing compounds contained in alumina production differs significantly (Table 1).

Table 1. Water solubility of Ca-containing compounds.

No.	**Compound**	**T, °C**	**Solubility, g/dm3**
1	$CaCO_3$	75	0.018
2	$2Ca(OH)_2$	100	0.770
3	CaC_2O_4 (oxalate)	95	0.014
4	$Ca_3(PO_4)_2$	25	0.020
5	Ca-salt of malic acid	37.5	4.51
6	$3CaO \times Al_2O_3 \times xH_2O$	-	N/a

Investigation of the effect of various factors on solubility of calcium, expressed in terms of $Ca(OH)_2$ (g/dm^3) demonstrated:

- total content of C_{org} in liquor at a level of 12–14 g/dm^3 leads to increase in solubility of CaO in liquor having composition similar to UAZ spent liquor to 0.03 g/dm^3. Salts of humic acids have a similar effect;
- reduction in sodium carbonate content in alkaline aluminate liquor also leads to substantial increase in CaO solubility (by~ 2 times), which can be easily explained by the lack of reaction of calcite formation having a lower solubility;
- increase in NaOH concentration leads to an increase in CaO solubility (up to 2 times).

It is reputed that in the course of TCA synthesis CaO solubility substantially increases, since practically all CO_3^{2-}ions are removed from liquor in the form of CHCA, and the whole content of sodium is converted to caustic (NaOH). Against this background, solubility of organic calcium compounds increases.

When forming the TCA filter bed, the content of dissolved CaO in liquor at a level of 0.03 – 0.04 g/dm^3 is normal and is caused by net solubility. This is one of the causes for calcium leakage into product liquor when formation of TCA layer on filter cloth is completed.

3. TCA Preparation Technology Adopted by UAZ as Compared to Best World Practices

In 2006-2008, Institute of Solid State Chemistry, Ural Branch of Russian Academy of Sciences (ISS UrB RAS) and Research & Development Company "MASHPROM" JSC conducted at UAZ investigations aiming to optimize TCA preparation technology. The work included selection of conditions in a laboratory [4] and a cycle of field tests. On its basis, two areas of TCA synthesis for security filtration were retrofitted. The developed technology allowed to obtain TCA with average crystal size of about 10 μm in semi-field tests.

The following conditions were recommended:

- preparation of seed at a temperature of 96 °C for at least 4 hours to ensure complete conversion of CHCA into TCA, crystals coarsening, and preparation of liquor with high α_{caust} ratio that does not contain carbonates;
- introduction of green liquor and lime milk, providing weight ratio $CaO/Al_2O_3 \approx 1.6$;
- maintaining TCA synthesis process for filtering layer at a temperature at least 90 °C and for at least 2 hours with at least 30 % of seed;
- mechanical agitation of slurry in the course of TCA synthesis.

Due to a number of process limits, the temperature and CaO/Al_2O_3 ratio are not maintained in the synthesis. Thus, CaO/Al_2O_3 ratio decreased to 1.0 and lower, but even under these conditions TCA was obtained with average crystal size from 8.4 to 12.1 µm.

The potential of the technology developed by the ISS UrB RAS was not realized in a full scope due to the following circumstances:

a) to provide normal operation of existing filters in secure filtration, TCA concentration in feed slurry should be 40 – 60 g/dm^3, while in fact, concentration is at least 93 g/dm^3;

b) some difficulties arose with preparation of the required volume of lime milk for TCA production. Instead of the required single-time feed of lime milk in amount of at least 100 m^3, only 40 – 70 m^3 could be prepared for this purpose;

c) in the process of mixing it is not possible to maintain the temperature of slurry required for the process;

g) due to the fact that lime milk is also used in other production processes, its concentration in terms of CaO_{act} is in the range from 100 to 120 g/dm^3, which is insufficient;

e) in laboratory studies the effect of seed on particle size distribution of obtained TCA crystals was not determined.

For these reasons, actual content of -1.6 µm fraction in TCA produced at UAZ significantly exceeds 6 %, and actual content of +8.5 µm fraction is less than 30 %. In general, we can say that the technology of synthesis adopted at UAZ corresponds to the world practice. At the same time, the effect of some unaccounted factors precludes from obtaining TCA having particle size distribution in accordance with the process instructions:

- +8.5 µm fraction content ≥ 50 %;
- -1.5 µm fraction content – not exceeding 6 %.

An attempt was made to establish the factors having an impact on TCA synthesis at UAZ and to propose some adjustment in the process for achieving target parameters.

4. Experimental

4.1. Effect of CaO/Al_2O_3 Ratio and Liquor Composition on Synthesis of Seed and TCA

Conditions of the Experiment. For the investigations three liquors were prepared derived from UAZ production evaporated spent liquor:

- green liquor;
- spent liquor;
- mixture of spent and green liquors in a ratio of 1:1 (by volume).

Concentration of the liquors approximately corresponded to composition of UAZ production liquors (Table 2).

Table 2. Composition of liquors used for TCA synthesis.

Liquor No	**Name of liquor**	**Composition, g/dm^3**					**$\alpha_{к}$**
		Al_2O_3	**Na_2O** caust	**K_2O** caust	**Na_2O** carb	**K_2O** carb	
1	Spent liquor	64.8	144.2	-	15.9	-	3.66
2	Green liquor	125.0	133.1	-	14.0	-	1.75
3	Green liquor + spent liquor (50:50)	94.9	138.7	-	14.95	-	2.40
4	Green liquor + spent liquor (50:50) – carbonate-free	99.6	145.3	-	traces	-	2.4
5	Sodium aluminate liquor	89.3	117.8	-	18.0	-	2.17
6	50 % sodium and 50 % potassium aluminate liquors	92.8	60.45	91.65	8.0	9.0	2.14
7	Potassium aluminate liquor	90.2	-	182.1	-	18.0	2.19

In all experiments, the purchased lime from the UAZ supplier was used (Table 3). Lime activity after additional burning was 96 % in terms of CaO_{act}. Incompletely burned material was separated by sieving the resulting lime milk through a 160 µm sieve.

Table 3. Composition of UAZ lime used in experiments of TCA synthesis.

Chemical composition, wt. %												
SiO_2	**Al_2O_3**	**Fe_2O_3**	**TiO_2**	**P_2O_5**	**CaO**	**MgO**	**Na_2O**	**K_2O**	**V_2O_5**	**Cr_2O_3**	**MnO**	**SO_3**
1.6	0.99	0.47	0.1	<0.02	95.7	1.1	<0.15	<0.15	<0.015	<0.01	0.02	0.1

For preparation of lime milk, lime was boiled in distilled water at a temperature of 90 – 96 °C to obtain lime milk with CaO_{act} in the range of 110 – 120 g/dm^3.

Preparation of seed and TCA. Before carrying out the experiments, TCA seed was prepared by mixing one of the liquors (1, 2, 3) and prepared lime milk in ratios: $CaO/Al_2O_3 = 0.20$; 0.25; 0.30. Synthesis of seed and TCA was carried out at a temperature of 96±1 °C in a thermostat with an agitator. Lime milk was fed in three stages within 15 minutes by equal portions. The temperature of lime milk at feeding was +60±2 °C. All the time the reactor was in the thermostat, therefore at the end of dosage the temperature in it was 95 – 96 °C. Hence, time marking of synthesis started immediately after completion of lime milk feeding. After completion of lime milk feeding, TCA was held for 60 minutes with continuous mechanical stirring (50 rpm) at a temperature of 96±1 °C. In TCA synthesis for filter bed, the holding time was 2 hours. The samples selected for analysis after filtration and "squeezing" on a Buchner funnel and washing with hot H_2O_{dist} were preserved by mixing with alcohol in a weighing bottle and directed for determination of particle size distribution. The samples for phase composition were "squeezed out" after washing, dried on a filter and directed to X-ray phase analysis.

The obtained products were analysed for:

- particle size distribution with the use of laser particle analysers SILOS and Microsizer-201. The TCA samples collected after the experiments were placed in a receiving chamber of a sample preparation block filled with water. An agitator, constantly operated during the analysis, mixed TCA with distilled water. In the course of analysis suspension from the cuvette circulated in a closed loop. To prevent settling and sticking of particles during analysis, the suspension was exposed to ultrasound for 30 seconds. Chemical dispersant was not added;
- semi-quantitative X-ray phase composition was analyzed for unreacted CaO, $Ca(OH)_2$, formation of calcium hydrocarboaluminate, TCA, calcite

XRD analysis was done using PANalytical X'Pert Pro XRD analyser (with MPD thermochamber that allows to trace phase transitions online at heating of powders from 300 °C to 1300 °C). The unit is equipped with ceramic tube with cobalt anode and has scan speed 1°/sec.

In the experiments for TCA preparation, all three liquors were used, with preliminary preparation of seed based on liquors No 1 – 3 and subsequent use of these seeds in amount of 30 and 50 % (from the total liquor volume + lime milk) in TCA preparation. In these experiments, lime milk was fed in a ratio: $CaO/Al_2O_3 = 0.53$ (actual UAZ situation) and 1.6 (recommended by Institute of Chemical Technology, UrB RAS).

Data analysis revealed the following dependencies:

- increase in the ratio CaO/Al_2O_3 from 0.2 to 0.3 during seed synthesis has a positive effect on the size of produced TCA;
- due to an increase in the ratio of CaO/Al_2O_3 from 0.53 to 1.6 in the synthesis of TCA, a significant amount of lime remains unreacted being "encapsulated" under a layer of CHCA and TCA. In this regard, it is advisable for more efficient use of lime to reduce CaO/Al_2O_3 ratio to 1.3 – 1.4.
- increase in the ratio (CaO/Al_2O_3 from 0.53 to 1.6) in the synthesis of TCA causes emergence of calcium hydrocarboaluminate precipitates in a significant amount with a small amount of calcite;
- high CaO/Al_2O_3 ratio in slurry and the use of liquor having low α_{caust} ratio (mixture of green and spent liquors) approached the target values in reducing minus 1.5 µm fraction content and achieving at least 50 % of ≥ 8.5 µm fraction content
- 30 % of seed at vigorous stirring is sufficient to maintain parameters of TCA synthesis.

The following conditions were recommended:

- preparation of seed: temperature 96 °C for at least 1 hour (without considering time of gradual (fractional) lime milk introduction) and CaO/Al_2O_3 weight ratio at least 0.3;
- seed in amount of 30 % is sufficient for synthesis of filter media (TCA);
- synthesize TCA with the use of a mixture of aluminate and spent liquors;
- dose lime milk using a weight ratio $CaO/Al_2O_3 \approx 1.35$;
- synthesis process at a temperature of at least 90 °C and for at least 2 – 4 hours while stirring.

4.2. The Impact of Potassium in Liquors on TCA Synthesis

Three synthetic aluminate liquors were prepared (liquors 5 – 7 in Table 2). The sequence of TCA synthesis was as follows:

Seed preparation. TCA seed was prepared by mixing one of the liquors (1, 2 or 3, Table 2) and prepared lime milk in a ratio: $CaO/Al_2O_3 = 0.35$. The synthesis of seed was carried out in a thermostat with an agitator at a temperature of 96±1 °C. The amount of seed was 30 % of the amount of TCA being synthesised.

Preparation of TCA. Synthesis of TCA was carried out at a temperature of 96±1 °C in a thermostat with an agitator. Green liquor was fed into slurry seed, and then lime milk was fed for 15 minutes in three stages, by equal portions. The temperature of lime milk being fed was 60±2 °C. Lime milk (further LM) was fed for 15 minutes while the container was in the thermostat, hence at the end of feeding the temperature was +95 – 96 °C. Initial timing for TCA synthesis started immediately upon completion of LM feeding. After LM feeding, the resulting TCA suspension was held for 120 minutes with continuous mechanical stirring by a propeller agitator (50 rpm). Table 4 shows particle size distribution of the resulting seeds and TCA.

Table 4. The impact of potassium alkali on particle size distribution of the synthesised TCA*.

Exp. No	Sample interpretation	Weight fraction of particles (P, %) corresponding to the target values of particle sizes							
		Particle size D, µm							
		1.5	1.6	3	5	8	15	30	40
1	Seed (sodium aluminate liquor)	**12.4**	13.2	24.9	43.2	**65.1**	90.8	99.3	100
	Synthesis – holding time 120 min.	**21.7**	23	40.7	64.1	**79.6**	94.6	99.6	100
2	Seed (50 % sodium and 50 % potassium aluminate liquor)	**14.0**	15	29.3	53.9	**75.4**	94	99.6	100
	Synthesis – holding time 120 min.	**24.6**	26.1	45	68.1	**81.0**	94.8	99.6	100
3	Seed (potassium aluminate liquor)	**11.6**	12.2	22.2	33.6	**54.4**	87.3	99.1	99.8
	Synthesis – holding time 120 min.	**28.1**	30.1	52.7	74.1	**84.1**	95.5	99.7	100

Note: * Particle size distribution analysis was performed with the use of Microsizer-201

As can be seen from Table 4, an increase in potassium content in the liquor leads to an insignificant decrease in - 8 µm fraction content. Therefore, the presence of K_2O in an amount of 30 – 40 g/dm^3 in UAZ Bayer liquors is not the main reason for synthesis of fine TCA.

4.3. The Impact of Sodium Carbonate Content in Liquor

To determine the effect of sodium carbonate in alkaline-aluminate liquor on particle size distribution of synthesised TCA, experiments were carried out to synthesize TCA in carbonate soda-containing and -free liquors.

Synthetic liquor No. 4 (Table 2) was prepared, which is an analogue of liquor No. 3, i.e. mixture of UAZ production spent liquor and aluminate liquor in a ratio of 1:1 (by volume).

Based on carbonate soda-free liquor No 4, experiments were carried out to synthesize TCA under the following conditions with addition of seed in amount of 30 and 50 % (Tables 5 and 6).

Table 5. Semiquantitative phase composition of the resulting TCA precipitates.

Exp. No	Conditions of experiment	Phase composition	Main lines intensity (imp./sec.)			
			C_3AH_6, 2.28 Å	$Ca(OH)_2$, 2.63 Å	$CaCO_3$, 3.035 Å	CHCA 7.56 Å
29	**Seed** **liquor without $Na_2O_{carb.}$** spent + alum./(1:1) + lime milk (CaO/Al_2O_3= 1.6)	Mainly C3AH6, $Ca(OH)_2$, rare traces of CHCA*	4,040	675	-	rare traces
30	**Liquor without Na_2O_{carb}** 30 % seed + spent + alum. (1:1) + lime milk (CaO/Al_2O_3 =1.6)	Mainly C3AH6, $Ca(OH)_2$, CHCA*	4,260	600	-	370
31	**Liquor without Na_2O_{carb}** 50 % seed + spent + alum. (1:1) + lime milk (CaO/Al_2O_3=1.6)	Mainly C3AH6, $Ca(OH)_2$, CHCA*	4,295	640	-	245

Note: * CHCA – calcium hydrocarboaluminate $3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}11H_2O$

Table 6. Particle size distribution of TCA produced from soda-free liquor*.

Exp. No	Sample interpretation and conditions of experiment	D average	Particle size distribution, cumulative values, μm/%											
			-0.3	-1	-1.6	-2	-3	-5	-8	-10	-15	-20	-30	-40
29	Seed spent + alum. (1:1) + lime milk CaO/Al_2O_3=1.6	9.8	1.75	8.7	**13.8**	16.05	20.2	30.38	**46.7**	57.0	78.8	90.6	97.9	99.8
30	30 % seed + spent + alum. (1:1) + lime milk CaO/Al_2O_3=1.6	9.7	1.65	8.4	**13.6**	15.89	20.3	31.05	**48.4**	59.22	79.6	90.3	98.2	99.9
31	50 % seed + spent + alum. (1:1) + lime milk CaO/Al_2O_3=1.6	9.7	1.89	8.8	**13.8**	15.98	20.2	30.25	**47.4**	58.1	78.1	89.9	99.1	100

Note: * Particle size distribution analysis was performed with the use of SILAS.

The absence of soda in the liquor during synthesis enables production of TCA practically without an intermediate phase – CHCA, but there remains a significant amount of $Ca(OH)_2$, possibly encapsulated inside the TCA particles (Table 5).

The absence of soda in liquor practically does not reduce the content of -1.6 μm fraction, but increases +8 μm fraction content to 52 % (Table 6).

4.4. Testing the Effect of Polysugars -Based Flocculant (HF1110 Solvay-Cytec) Additive on TCA Synthesis

As recommended by the flocculant producer, Solvay-Cytec Company, experiments were carried out with addition of a flocculant based on low molecular weight organics – polysugars (HF1110). The technique of experiments was as follows:

The seed was prepared according to a conventional scheme with CaO/Al_2O_3 ratio of 0.3. Synthesis of TCA was performed based on liquor No 3 (Table 2). Flocculant HF1110 was added into the prepared lime milk in amount of 100 g per tonne of TCA being synthesized. Lime milk with CaO_{act} content about 100 – 120 g/dm^3 was dosed to achieve CaO/Al_2O_3 ratio = 1.6 at temperature of 96±1 °C to a reactor with an agitator placed in a thermostat. The amount of seed in experiments was 30 and 50 %.

Lime milk was fed for 15 minutes in three stages. The temperature of lime milk was 60±1 °C. After completion of lime milk feeding, the resulting TCA suspension was held for 60 minutes with continuous mechanical stirring (50 rpm) at a temperature of 96±1 °C.

The obtained products were analysed for phase composition and particle size distribution. Analysis of the results demonstrated that addition of a polysugars-based flocculant to lime milk makes it possible to increase +8 μm fraction content that is probably due to an increase in solubility of calcium.

5. Conclusion

1. The investigation carried out to clarify conditions of synthesis of tricalcium aluminate for security filtration at UAZ enabled to clarify conditions and recommend a number of improvements:

- 30 % of seed of the amount of TCA being synthesized is sufficient; further increase to 50 % has no significant effect;
- it is recommended in seed synthesising to have CaO/Al_2O_3 weight ratio at least 0.3;
- it is recommended to conduct TCA synthesis with spent liquor or mixture of green and spent liquors. The decrease in concentration of caustic alkali and alumina in the liquor gives a positive effects on particle size distribution of TCA being synthesized;
- in TCA synthesis, it is necessary to have the highest possible CaO/Al_2O_3 weight ratio, it is recommended to come back to the weight ratio ≈ 1.35.

Compliance with these conditions will allow obtaining material for filter bed that meets the requirements of UAZ process control chart in respect of particle size distribution:

- +8.5 µm fraction content ≥ 50 %;
- -1.6 µm fraction content – not exceeding 6 %.

2. Investigation of the effect of some factors on resulting TCA composition demonstrated:

- increased content of potassium in UAZ Bayer liquors has an insignificant effect on TCA size degradation;
- TCA synthesis from liquor having low sodium carbonate content makes it possible to prevent formation of intermediate products (calcium hydrocarboaluminates), i.e. TCA is directly synthesized with cubic syngony, but it practically does not affect particle size distribution. This fact cast some doubt on the determining effect of intermediate phases on particle size of the resulting TCA;
- addition of polysugars to lime milk during synthesis has a positive effect on TCA particle size distribution.

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