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 $1.5 - 2 \mu m$); 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/Al₂O₃ 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 (C₃AH₆) 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/Al₂O₃ 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, airslaked 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:Al₂O₃ 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:Al₂O₃ 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;
- Al₂O₃ and Na₂O total concentrations in liquor, with respect to free caustic alkali;
- availability in liquor of Na₂CO₃ and other inorganic impurities Na₂SO₄, 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 $\leq 1.5-2 \ \mu m$;
- 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

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/Al₂O₃ 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/Al₂O₃ 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 μ m fraction content \geq 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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7. References

- 1. N.V. Kuznetsova, A.M. Kuvyrkina, A.G. Suss, et.al. The effect of magnesium salts on resulting TCA and possibility of using of obtained compounds in digestion of bauxite, *Non-ferrous metals*, 2008, No. 11, p. 63-68.
- 2. S.L. Barham, S.U. Khan, J.T. Malito, W.J. Rennick Optimization of tricalcium aluminate for enhanced Bayer liquor filtration, *Light Metals*, 2000, pp. 111-116.
- 3. B.I. Whittington, T.M. Fallows, M.J. Willing Tricalcium aluminate hexahydrate (TCA) filter aid in the Bayer industry: factors affecting TCA preparation and morpholog", *International Journal of Mineral Processing (ELSEVIER)*, 49 (1997) 1-29.
- 4. O.D. Linnikov, V.A. Nikulin, V.L. Podberyozny, M.A. Perestoronina, etc. Production of coarse-crystalline tricalcium aluminate, *Non-ferrous metals, 2006*, No. 2, p. 49-51.)
- 5. P.V. Yashunin, N.I. Eryomin About composition of calcium hydroaluminates formed in interaction of alkaline aluminate liquors with lime, *Non-ferrous metals*, *1968*, No. 12, p. 57-59.

- 6. B.I. Whittington, C.M. Cardile (CSIRO) The chemistry of tricalcium aluminate hexahydrate relation to the Bayer industry, *International Journal of Mineral Processing (ELSEVIER)*, 48 (1996) 21-38.
- 7. M.S. Crowley Effect of starting materials on phase relations in the system CaO-Al₂O₃-H₂O, *Journal Am. Ceram. Soc.*, 47: p. 144-148, 1964.
- 8. R.B. Pepler and L.S. Well The system CaO-Al₂O₃-H₂O from 50 to 250 °C, *Journal Res. Natl. Bur. Stand., 52*: p. 75-92, 1954.
- 9. E. Schultze-Rhonof On the chemistry of bauxite extraction II. Studies in the system Na₂O-CaO-TiO₂-Al₂O₃-H₂O between 100 and 275 °C, *Z. Anorg. Allgem. Chem.*, 369: p. 303-307, 1973.
- 10. J. Zambo and M. Orban-Kelemen CaO and MgO compound formation in processing calcium-dolomite bearing bauxites by the Bayer method, *Acta Tech. Acad. Sci. Hung.*, 82: p. 333-352, 1976.
- 11. Lawrence Joseph Andermann, Geoffrey Joseph Pollet The manufacture of tricalcium aluminate, *Light Metals*, 2003, pp. 11-17.
- 12. Reza Salimi and James Vaughan Crystallisation of tricalcium aluminate from sodium aluminate solution using slaked lime, *Powder Technology*, 294 (2016), pp. 427-483.
- 13. A.J. Perotta and F. Williams "Hydrocalumate formation in Bayer liquor and its promotional effect on oxalate precipitation", *Light Met.*, 1995, pp. 77-87.
- 14. B. Xu "Lime chemistry in the Bayer process", *Ph.D. thesis, Murdoch University*, Perth, 1991.
- 15. V.M. Sizyakov, M.N. Smirnov Comparative stability of hydrogarnets and tricalcium aluminate in caustic liquors at 30-90 °C, *Non-ferrous metals*, *1969*, 42(10), p. 59-61.
- 16. P.J. The and T.J. Sivakumar The effect of impurities on calcium in Bayer liquor, *Light Met.*, *1985:* 209-222.
- 17. Mitsubishi Mining Cement (1988) Tricalcium aluminate hydrate particles manufactured by reacting calcium hydroxide with aluminium hydroxide in the presence of saccharose", *Jpn. Kokai Tokkyo Koho JP 01,270,509 [89,270,509] & Mitsubishi Mining Cement (1982)* Spherical particles of tricalcium aluminate hydrate, Jpn. Kokai Tokkyo Koho JP 57 118020.
- 18. J.F. Young Effect of organic compounds on the interconversion of calcium aluminate hydrates: Hydration of the tricalcium aluminate, *J. Am. Ceram. Soc., 1970*, 53(2): 65-69.
- 19. J.F. Young Effect of organic compounds on the interconversion of calcium aluminate hydrates. Hydration of the monocalcium aluminate, *Cem. Congr. Res., 1971*, 1: 113-122.