An Automated Reference-Free Rietveld-Method-Based X-Ray Diffraction Analysis of Cryolite Ratio

Petr S. Dubinin[1], Aleksandr N. Zaloga[2], Sergey D. Kirik[3], Igor S. Yakimov[4] and Oksana E. Bezrukova[5]
1. Research engineer
2. Research engineer
3. Professor
4. Professor
5. Research engineer
Siberian Federal University, Krasnoyarsk, Russia
Corresponding author: opiksina@gmail.com

Abstract

In most aluminum smelters, cryolite ratio (CR) is normally measured automatically using X-ray diffraction (XRD) quantitative phase analysis using calibration curves. However, two factors significantly reduce the accuracy of measuring CR by such methods. First, XRD analytical instruments need periodic calibration, which is performed using multiphase matrix reference materials of bath with a known quantitative phase composition. Creating such reference materials is a challenging task, because they should contain 4 – 6 fluoride phases, whose concentrations are accurately certified. Second, the calibrated methods do not consider variations of microcrystalline and atomic structure of phases in real solid bath samples. Thus, using reference-free full-profile Rietveld method instead of conventional XRD methods for measuring CR is advantageous for the process control because it does not use calibration and refines the crystal structure of bath samples. However, the Rietveld method is interactive and needs automation for implementing in the process control. If so, the method automatically refines preset approximate values of profile and structural parameters of the crystalline phases and then calculate CR from the quantitative phase composition. The problem is the preset of adequate approximate parameter values that are accurate enough to be refined automatically. We developed a new method to address this problem. The essence of the method is an automatic search of the initial approximate values by a genetic algorithm (GA) followed by the Rietveld refinement of the found values. The accuracy of the automatic analysis of CR performed for 24 branch reference materials of bath is characterized with a standard deviation of 0.035 and can be improved by further developments in GA.

Keywords: Cryolite ratio, Rietveld method, process control, x-ray diffraction phase analysis, bath composition.

1. Introduction

Electrolyte in aluminum electrolysis cells constantly suffers from the destabilization of its chemical composition, which shifts from the optimum. The optimal composition of bath is maintained by adding fluorides in a cell. The amount of fluorides is calculated in accordance with the results of periodically performed express quantitative analysis of solid bath samples. A number of methods are used for this purpose, such as chemical analysis (CA), X-ray diffraction analysis (XRD), X-ray fluorescence analysis (XRF), thermal analysis, etc. Normally, electrolyte is the melt of Na-Al-Ca-F-O, and sometimes KF, MgF_2 or LiF are added. The chemical elements exist in the melt in the form of complex ions, whose composition changes during the electrolysis cycle. As so, an integral characteristic of the bath composition is the cryolite ratio (CR) – the ratio of molar concentrations of sodium fluoride and aluminum fluoride (Equation (1)):

$$CR = \frac{C(NaF),mol.\%}{C(AlF_3),mol.\%} = \frac{2C(NaF),wt.\%}{C(AlF_3),wt.\%} \quad (1)$$

where:
C(NaF) Concentration of sodium fluoride in electrolyte, mol. % or wt. %
C(AlF_3) Concentration of aluminum fluoride in electrolyte, mol. % or wt. %.

Bath ratio (BR) is also used to characterize bath composition, given by Equation (2), or excess AlF_3, as expressed in Equation (3):

$$BR = \frac{1}{2}CR \quad (2)$$

$$AlF_3ex = C(AlF_3) - \frac{1}{3}C(NaF) \quad (3)$$

where:
C(NaF) Concentration of sodium fluoride in electrolyte, wt. %
C(AlF_3) Concentration of aluminum fluoride in electrolyte, wt. %

CR, BR and AlF_3ex all indicate similar information about the bath composition.

The express process control of the electrolyte composition is generally performed by X-ray diffraction quantitative phase analysis (QPA), which uses calibration curves [1 – 3]. The cryolite ratio is calculated according to Equation (1). The concentrations of NaF and AlF_3 are calculated using the results of the QPA of crystallized bath samples. The concentrations of phases listed in Table (1), in turn, are calculated from the measured intensities of their diffraction peaks. The optimal frequency of measuring the CR is once every two days, the accuracy of the analysis is Δ(p = 0.95) ~ 0.04 (that is, ± 0.04 at 95 % confidence level), and the optimal measurement time per sample is several minutes.

Table 1. The phase composition of typical industrial bath samples at the Russian aluminum smelters.

Phase	Chemical Formula	Concentration range, wt. %	CR Range
Cryolite	Na_3AlF_6	0 – 90	> 1.67
Chiolite	$Na_5Al_3F_{14}$	0 – 85	< 3.0
Sodium fluoride	NaF	0 – 5	> 3.0
Ca-cryolite 1	$NaCaAlF_6$	0 – 15	< 3.0
Ca-cryolite 2	$Na_2Ca_3Al_2F_{14}$	0 – 20	< 2.95
Fluorite	CaF_2	0 – 9	> 2.45
Weberite	Na_2MgAlF_7	0 – 15	< 2.85
Neiborite	$NaMgF_3$	0 – 6	> 2.5
α–, β–, γ– alumina	Al_2O_3	2 – 5	

However, two factors significantly reduce the accuracy of measuring CR using calibration curves. First, XRD analytical instruments need periodic calibration, which is performed using multiphase matrix reference materials of bath with a known quantitative phase composition [4, 5]. Creating such reference materials is a challenging task because they should contain 4 – 6 fluoride phases, whose concentrations are accurately certified. Second, the calibrated methods do not consider variations of microcrystalline and atomic structure of phases in real solid bath samples. Thus, using reference-free full-profile Rietveld method [6] instead of conventional XRD methods for

References

51. Bingliang Gao et al., Determination of Cryolite Ratio of Aluminum Electrolytes, *Light Metals* 2010, 569-573.
52. Indah Tjahyono Nursiani et al., Improvin XRD analysis for complex bath chemistries – investigations ang challenges faced, *Light Metals* 2014, 573-578.
53. Oksana Piksina et al., Combined control of aluminum bath composition by X-ray diffraction and X-ray fluorescence analysis, *X-Ray Spectrometry,* Vol. *46*, № 5, (2017), 474-482.
54. Electrolytic Bath Standards, Alcan International Ltd., Quebec, Canada (2005).
55. Igor S. Yakimov et al, Development of branch reference materials of aluminum bath, *Reference Materials,* № 4, (2008), 34-42.
56. D.L. Bish, S.A. Howard, Quantitative phase analysis using the Rietveld method, *J.Appl., Cryst.,* № 21, (1998), 86-91.
57. Sergey D. Kirik, Igor S. Yakimov, An evaluation of XRD and XRF methods used in aluminium bath analysis, *Advances in X-ray Analysis,* Vol. *44*, (2001), 85-90.
58. Frank R. Feret, Breakthrough in Analysis of Electrolytic Bath Using Rietveld-XRD Method, *Light Metals* 2008, 343-346.
59. Karsten Knorr. Present progress in fast XRD analysis applying the Rietveld method for bath control, *The 19th International Symposium and Exhibition of ICSOBA*, Bélem, Brazil, 30 – 31 October 2012, Paper AL24.
60. Uwe König, Nicholas Norberg, Process Control in Aluminium Industry - News in the XRD Tool Box, *Proceedings of 35th International ICSOBA Conference*, Hamburg, Germany, 2 – 5 October 2017, *Travaux 46*. Paper AL34, 1129-1134.
61. Julia N. Zaitseva, Physicochemical aspects of the analytical control of aluminium bath composition, *PHD thesis*, Krasnoyarsk, 2010, 156 p.
62. Hexiong Yang, Subrata Ghose, Dorian M. Hatch, Ferroelastic phase transition in cryolite, Na_3AlF_6, a mixed fluoride perovskite: high temperature single crystal X-ray diffraction study and symmetry analysis of the transition mechanism, *Physics and Chemistry of Minerals,* Vol. *19*, № 8, (1993), 528-544.
63. David E. Goldberg, *Genetic Algorithms in Search, Optimization, and Machine Learning*, Boston, MA, USA: Addison-Wesley Longman Publishing Co., Inc., 1989, 412 p.
64. Alexandr Zaloga et al., Genetic Algorithm for Automated X-Ray Diffraction Full-Profile Analysis of Electrolyte Composition on Aluminium Smelters, *Revised Selected Papers of Informatics in Control, Automation and Robotics 12th International Conference, ICINCO,* 2015, 79-93.
65. Eugene Semenkin, Maria Semenkina, The Choice of Spacecrafts' Control Systems Effective Variants with Self-Configuring Genetic Algorithm, *Informatics in Control, Automation and Robotics: Proceedings of the 9th International Conference ICINCO 2012*, Rome, Italy, 2012, Vol. 1, 84-93.
66. Eugene Semenkin, Maria Semenkina, Self-configuring Genetic Algorithm with Modified Uniform Crossover Operator, *Advances in Swarm Intelligence. Lecture Notes in Computer Science 7331*, Springer-Verlag, Berlin Heidelberg, 2012, 414-421.
67. *Inorganic Crystal Structure Database* (ICSD), http://www2.fiz-karlsruhe.de/icsd_publications.html.