AL09 - Comparative Study of Alumina Dissolution in Complex Aluminum Electrolytes

Bing-liang Gao[1], Fei He[2], Gang Li[3], Sheng-yi Wen[4], Ai-min Liu[5] and Zhao-wen Wang[6]
1. Full professor,
5. Assistant professor,
6. Full professor,
School of Metallurgy, Northeastern University, Shenyang, China
2. Chief Technology Officer,
3. Director of Reduction technology,
4. Director of Analysis center of smelter,
Zunyi Aluminum Co., Ltd., Zunyi, China
Corresponding author: blgao@mail.neu.edu.cn

Abstract

In northern Chinese aluminum smelters, the electrolyte has high content of lithium fluoride and low content of potassium fluoride. In southern Chinese aluminum smelters, the electrolyte has high content of potassium fluoride and low content of lithium fluoride. In this paper, alumina dissolution behavior in three kinds of electrolytes, including simple electrolyte, high lithium low potassium electrolyte and high potassium low lithium electrolyte, was studied. The effect of bath superheat on alumina dissolution was also discussed.

Keywords: Alumina dissolution, aluminum electrolysis, complex electrolyte.

1. Introduction

Since 2001, China has been the largest primary aluminum producer in the world. In 2019, China produced 35.044 million tonnes of primary aluminum and 72.4742 million tonnes of smelter grade alumina and imported 1.65 million tonnes of alumina [1]. Even though the portion of imported bauxite for alumina refining is continually increasing in recent years, at least 40 % alumina was produced from domestic bauxite, which mainly mined in Shanxi province, Henan province, Guizhou province and Guangxi province in China. Table 1 lists the contents of impurities, mainly oxides of alkali metals in domestic alumina. Compared to imported alumina, all domestic alumina contains high content of lithium oxide and potassium oxide. Domestic alumina A and Domestic alumina B are produced by alumina refining plants located in southern part of China. Domestic alumina C and Domestic alumina D are produced by some northern refining plants in China.

Table 1. Concentration of alkali oxides in domestic alumina and imported alumina [2].

Alkali oxides	Domestic A	Domestic B	Domestic C	Domestic D	Imported
K_2O, wt.%	0.048	0.016	0.029	0.027	0.002
Li_2O, wt.%	0.017	0.006	0.058	0.044	0.001

When domestic alumina is fed to the reduction cell, the concentration of lithium and potassium will gradually increase to some levels in the cryolite-based electrolyte. Many Chinese smelters do not have long-term alumina supplier. They usually feed cells with alumina from different sources, which always results in complex situation for engineers to control their cells. In China, there are several types of electrolytes according to lithium and potassium concentration in the bath:

- Simple electrolyte without lithium and potassium, referred to as SE;

- High lithium and low potassium electrolyte, typically, 5-8 % LiF and 2-3 % KF, referred to as HLE;
- High potassium and low lithium electrolyte, typically, 5-6 % KF and 1-2 % LiF, referred to as HPE;
- High lithium and high potassium electrolyte, typically, 4-5 % KF and 5-6 % LiF, referred to as HLPE

Many papers have discussed the poor performance of the cells operated with complex electrolyte. Table 2 lists some performance indicators of Chinese smelters using complex electrolytes. Even though some smelters claimed lower energy consumption, their cells are operated with low current efficiency.

Table 2. The key performance indicators of 500 kA reduction cells using complex electrolytes in China.

Smelters	**A**	**B**	**C**	**D**	**E**	**F**
kA	500	510	500	505	500	500
AL/cm	32-37	29-32	30-32	23-25	28-30	29-31
BL/cm	15-18	17-20	14-16	16-18	18-20	16-18
T/°C	900-915	905-915	945-955	955-965	945-955	950-965
CR	2.7-3.1	2.5-2.7	2.5-2.7	2.5-2.7	2.3-2.5	2.4-2.6
Al_2O_3%	2-3	2-3	2-3	2-3	2-3	2-3
KF%	2.7	3.2	4.5	1.4	-	-
LiF%	8.4	8.6	2.78	1.1	-	-
MgF_2%	0.3	0.5	0.42	0.3	5.0	0.3
CaF_2%	4.2	4.2	4.07	3.8	3.0	5.5
CV/V	4.09	3.97	3.93	3.91	4.00	4.00
CE/%	**88**	**91.5**	**91.7**	**89.5**	**92**	**91**
EC/kWh/kgAl	13.9	13.0	12.8	13.0	13.0	13.1

Note：AL-metal level；BL-bath level；T-bath temperature；CR-molar ratio of NaF/AlF_3；CV-cell voltage；CE-current efficiency；EC-DC energy consumption。

Many factors give their contributions to current efficiency, such as superheat control, anodic current distribution, MHD stability, and alumina dissolution behavior. In this paper, alumina dissolution behavior in various types of electrolytes was compared, and the effect of the superheat of bath on alumina dissolution behavior was also discussed.

2. Experimental

2.1 Chemicals

Analytical reagents, calcium fluoride, lithium fluoride, potassium fluoride and chemical pure reagent cryolite were dried for 2 h at 400 °C. Anhydrous aluminum fluoride was obtained by the following treatment of aluminum fluoride trihydrate: chemical pure reagent aluminum fluoride trihydrate mixed with ammonium hydrogen fluoride at mass ratio of 7:3 was dried for 3 h at 150 °C, 250 °C, and 500 °C, respectively. All the chemicals were kept in a dry box before use.

Primary alumina and secondary alumina (containing 0.55 wt% fluorine and 0.52 wt% carbon) used in the experiments were sampled from an aluminum smelter with an average grain size of 69.2 µm and 66.9 µm, respectively. The volume percent of fines (particle size smaller than 45µm) were 23.1 % in the primary alumina sample and 28.3 % in the secondary alumina sample. Alumina samples were dried at 300 °C for 24 h before use. The LOI (300-1000) of the primary alumina and secondary alumina were 0.8 wt% and 1.0 wt%, respectively.

Three types of electrolytes, SE, HLE and HPE, were used in this study. The compositions and corresponding liquidus temperatures are listed in the Table 3. The liquidus temperatures of these melts were determined by DTA method.

Table 3. The chemical compositions and liquidus temperatures of complex electrolytes used in the study.

No.	CR	Al_2O_3, %	CaF_2, %	KF, %	LiF, %	MgF_2, %	$T_{liquidus}$, °C	Type
1	2.1	2	4	0	0	0.3	950.9	SE
2		2	4	3	6	0.3	902.9	HLE
3		2	4	6	2	0.3	937.3	HPE
4	2.4	2	4	0	0	0.3	974.9	SE
5		2	4	3	6	0.3	919.5	HLE
6		2	4	6	2	0.3	945.1	HPE
7	2.7	2	4	0	0	0.3	986.5	SE
8		2	4	3	6	0.3	920.7	HLE
9		2	4	6	2	0.3	949	HPE

2.2 Experimental Method and Apparatus

The experimental apparatus for observing dissolution behavior was a see-through furnace, as shown in Figure 1. The crucible was made of high-purity quartz with a dimension of Ø 40 mm×100 mm. The crucible wall is 3 mm thick. Two quartz cells were put in the see-through furnace with three observing windows, two side-view windows and one bottom-view window. A sunlamp (JINBEI, EF-200VLED) was placed at the rear window to provide backlighting. A video camera (MV-VS078FC) close to the front window was used for recording the floating phenomena of alumina taking place inside the crucible, and another video camera close to the bottom window was used to record the dissolution of agglomerate of alumina rested on the bottom of the quartz crucible. A temperature controller (DWT-702) with a Pt-PtRh10 type thermocouple was used for measuring and controlling temperature of the furnace.

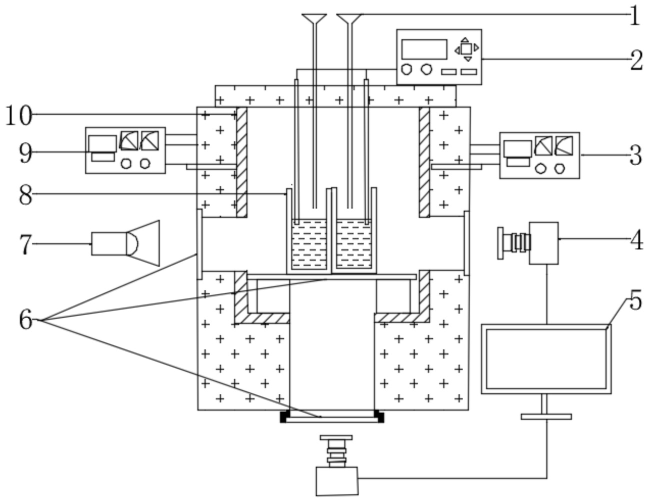

**Figure 1 The experimental apparatus of the transparent cell.
1- charging pipe; 2-temperature measurement module; 3,9-temperature controller; 4-camera; 5-computer; 6-quartz window; 7-light source; 8-quartz crucible; 10- Electric furnace.**

The weight of electrolyte in each run was 150 grams. The molten electrolyte height was 5.5 cm, and its temperature was controlled at a temperature of liquidus of the investigated bath + 10 (±1) °C during the experiments, giving the electrolyte an initial superheat of about 10 °C. 1.5 grams of primary alumina or secondary alumina was charged into the transparent molten salt each time through a corundum tube (length 500 mm, inner diameter 16 mm) whose end was 2 cm above the electrolyte surface. During every addition, the tube was dredged with a stainless-steel stick in case of blocking. The dissolution time of each feeding was counted from the moment when the alumina reached the surface of electrolyte till the bottom of the crucible became clearly visible. The next feeding was made when the temperature fluctuation of the melt was less than 1 °C in 10 minutes.

3. Results and Discussions

The video provided an excellent view of the alumina dissolution process. The dispersion of particles and agglomerates in the melt was clearly visible. Figure 2 shows snapshots of the dissolution of secondary alumina in HPE at different superheats. The secondary alumina floated on the surface of the melt first, and some of the alumina dispersed through the electrolyte and dissolved quickly in 20 seconds. The undissolved alumina particles formed a layer of white crust, which floated on the surface of the electrolyte for over 100 seconds. Then the crust sank to the bottom of the crucible and dissolved completely after 1000 seconds.

As shown in Figure 2, the floating time of the secondary alumina crust in HPE with superheat of 5 ºC is shorter than that of 10 °C, and vice versa the dissolution time of alumina. It took about 1016 s for alumina crust to dissolve into melt completely in HPE with superheat of 10 ºC, but 1346 s in HPE with superheat of 5 °C.

No stirring was applied in the experiments, so the dissolution time of alumina in aluminum electrolyte is significantly longer than that of situation with stirring or under industrial conditions [3]. Alumina dissolution behavior has close relationship with heat transfer and mass transfer status of the melt as reviewed by Pascal Lavoie, et al [4]. Static bath might provide a simplified condition for comparison of alumina dissolution behavior for alumina with different physical properties as well as in various types of electrolyte.

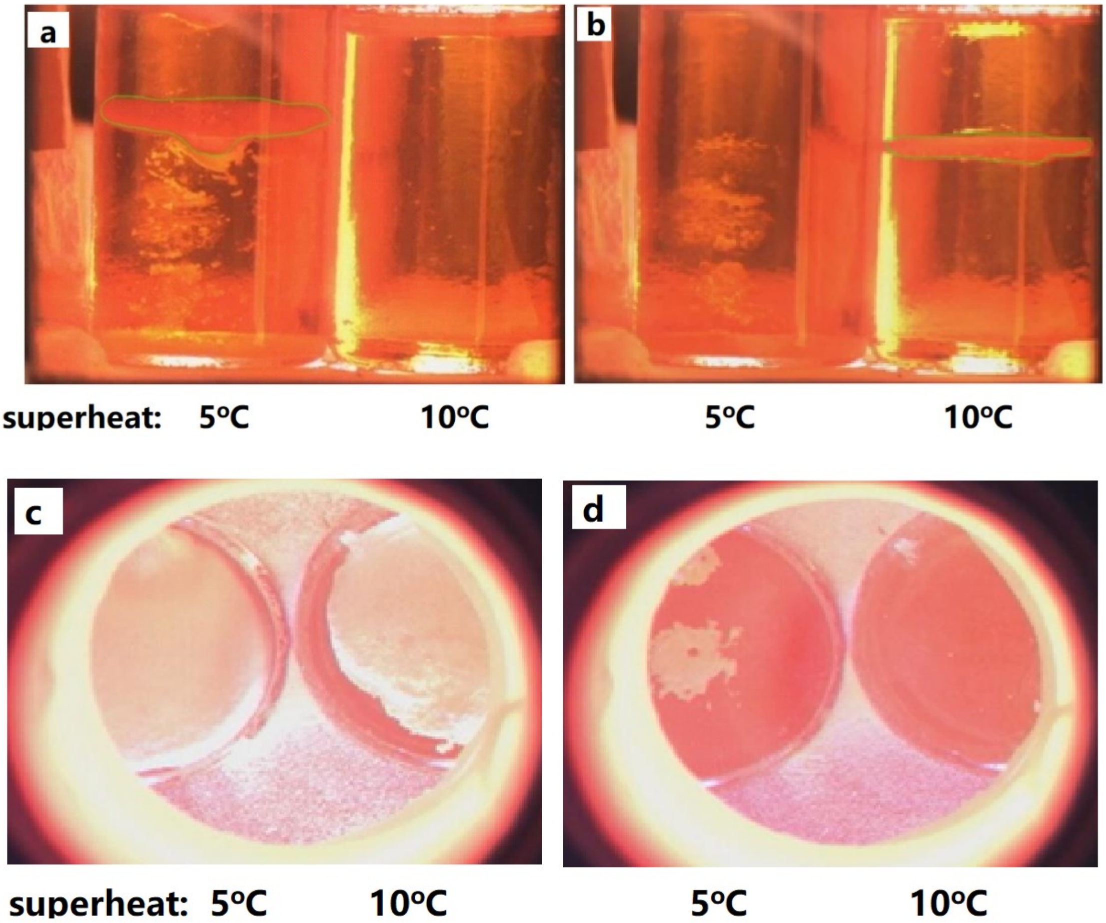

Figure 2. Snapshots of secondary alumina dissolution process in the HPE with CR = 2.7 at 954 °C (superheat = 5 °C) and 959 °C (superheat = 10 °C). (a)-at 32 s; (b)-at 110 s – side view; (c)-at 128 s; (d)-at 1016 s, bottom view.

In each experiment, the initial alumina concentration was set as 2 %, each addition of alumina increases the alumina concentration of 1 %. The dissolution rate of alumina is evaluated by two indicators: accumulative dissolution time and dissolution time for each addition. The accumulative dissolution time is the sum of dissolution times of several additions.

Figure 3 exhibits the alumina dissolution in SE with different cryolite ratios. Surprisingly, SE with high cryolite ratio did not exhibit significantly different dissolution behavior of secondary alumina. In both melts with low concentration of alumina, the dissolution time of secondary alumina were almost same for each addition of alumina. There was a small difference in melt with high concentration of alumina. Melt with high cryolite ratio exhibited slightly faster dissolution rate than that of melt with low cryolite ratio. According to literature [4], Kushel and Welch observed a doubling of dissolution time as the cryolite ratio decreased from 2.40 to 2.16. However, we did not observe so much dissolution time difference even the same tests were tried several times. The dissolution time for each addition might be different at same initial alumina concentration in these tests, but the time difference was not significant. These results indicate that bath chemistry has mild effect on dissolution behavior of alumina in SE if bath temperature is higher than 960 °C.

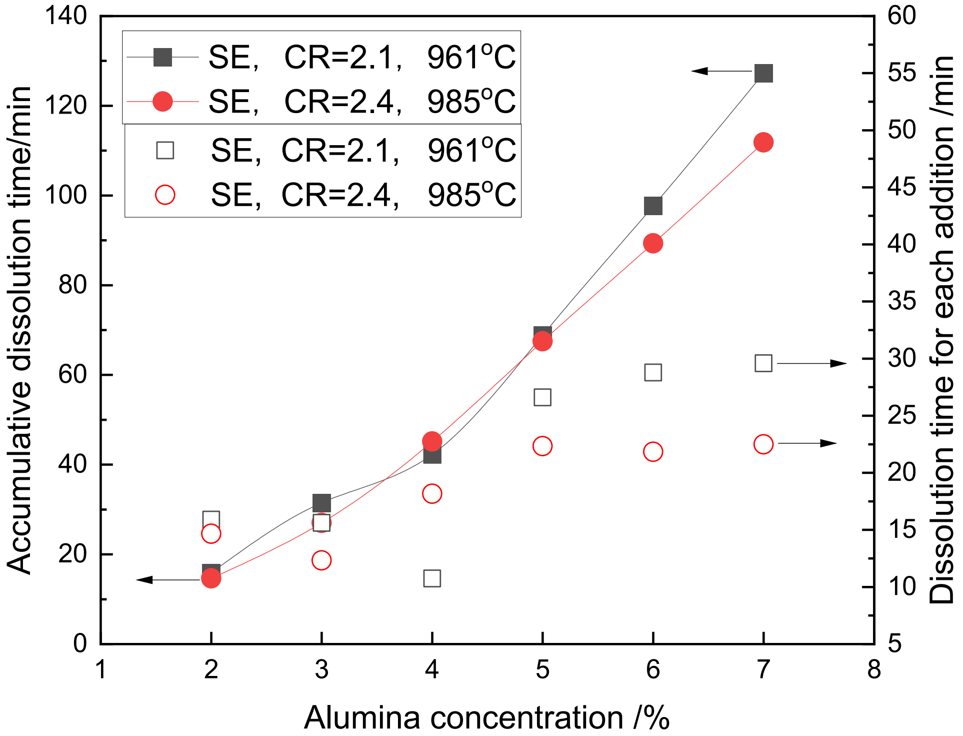

Figure 3. Accumulative dissolution time and dissolution time for each addition of secondary alumina in SE with different cryolite ratio.

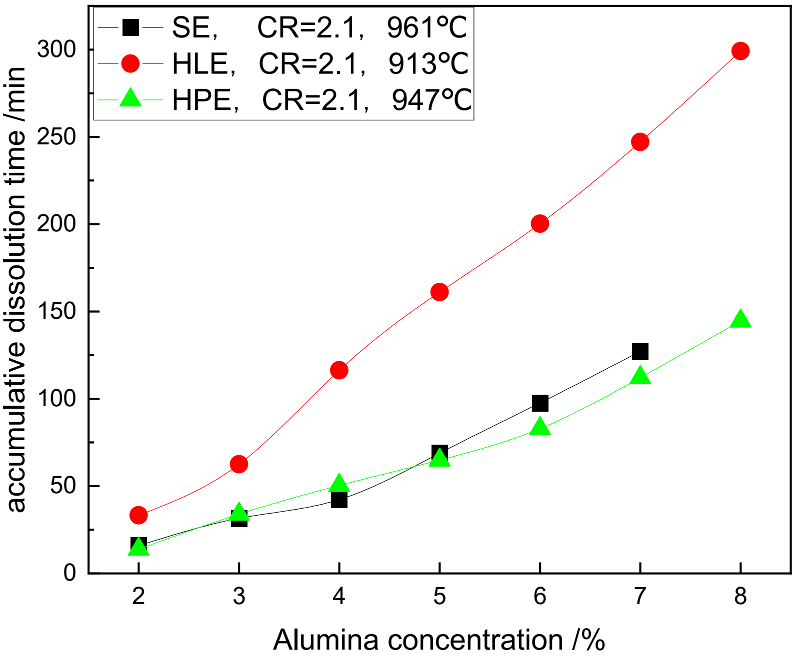

Figure 4. Comparison of the accumulative dissolution time of the secondary alumina in various types of aluminum baths.

Figure 4 exhibits the alumina dissolution behavior in various electrolytes. Evidently, the electrolyte with high concentration of lithium fluoride, referred to as HLE, shows the poorest dissolution ability for secondary alumina among three types of electrolytes. The dissolution rates of alumina in SE and HPE, respectively, are almost same. Because of the lowest liquidus temperature and lowest alumina saturation concentration compared to the other electrolytes, HLE shows the slowest dissolution rate among three types of electrolytes. Even though HPE has lower liquidus temperature, correspondingly lower operation temperature compared to that of SE, the dissolution rate of alumina does not exhibit much difference with that of SE. Combined with data shown in Figure 3, the effects of bath temperature and bath composition on the dissolution rate of alumina become weak if bath temperature is higher than 945 °C, especially in melts with low concentration of alumina.

Figure 5 exhibits the accumulative dissolution time of secondary alumina in HPEs with different cryolite ratio. Although the cryolite ratios of the HPEs change from 2.1 to 2.7, the liquidus temperatures of the melts increase 12 °C only. Three tested melts have close bath temperatures. Among these melts, HPE with cryolite ratio of 2.7 exhibited the fastest average dissolution rate, and HPE with cryolite ratio of 2.1 has the slowest average dissolution rate. However, the difference between them is not significant.

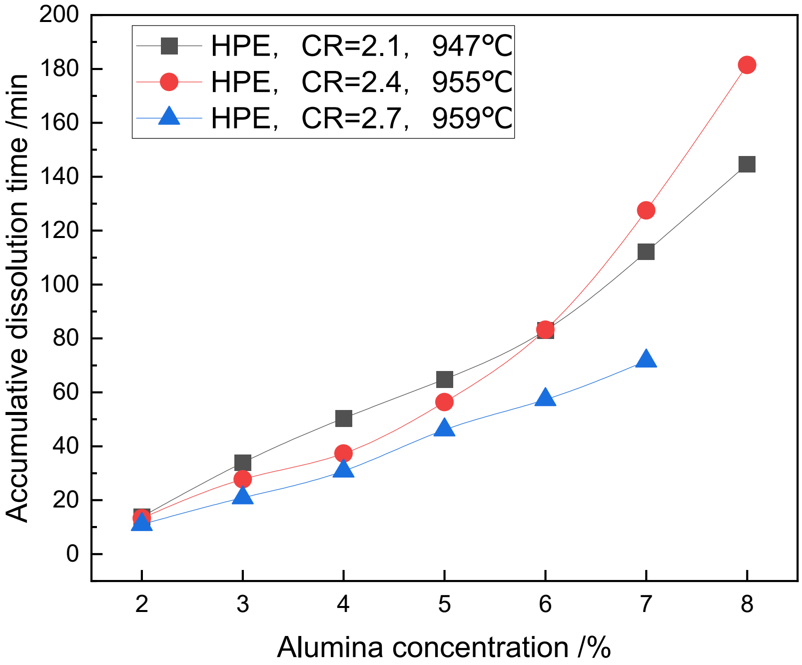

Figure 5. Comparison of the cumulative dissolution time of the secondary alumina in HPEs with different cryolite ratio.

Figure 6 exhibits the accumulative dissolution time of secondary alumina in HLEs with different cryolite ratio. The liquidus temperatures of the HLP with cryolite of 2.1 is 903 °C, the lowest one among three tested HLP melts, correspondingly the lowest test temperature. The rest HLEs have close liquidus temperatures, 919.5 °C for CR = 2.4, 920.7 °C for CR = 2.7 and correspondingly almost same test temperatures. As expected, alumina exhibited the slowest dissolution rate in HLE with cryolite ratio of 2.1 because of its lowest temperature and saturation concentration of alumina [5]. Surprisingly, results indicate that the HLE with CR = 2.4 showed slightly better alumina dissolution ability than that of HLE with CR=2.7. The liquidus temperatures of investigated melts adopted in the experiments were determined before tests, not deduced from published equations. According to the liquidus equation given by Solheim [6], the liquidus temperatures of HLEs are 918 °C for CR = 2.4 and 922 °C for CR = 2.7. As a result, the corresponding superheats are 13 °C for melt with CR = 2.4 and 9 °C for melt with CR = 2.7. We are not sure whether the superheat difference is the key reason for the above observed phenomena. On the other hand, the data analysis method adopted in this paper might be not good enough to tell the small difference of alumina dissolution behavior between tests. The experimental method and data analysis need to be improved in the future study.

According to Xiangwen Wang's investigation, alumina properties have big impact on dissolution behavior [3]. Therefore, different alumina used for tests might result in different dissolution behavior. In this investigation, the adopted primary alumina and secondary alumina have high content of potassium oxide. The tests confirmed that they are sensible to bath superheat. Fast dissolution would not be guaranteed if the bath superheat was less than 5 °C. An imported sandy alumina was tested for comparison and did not follow the same behavior. Bath superheat had little effect on dissolution time of this sandy alumina.

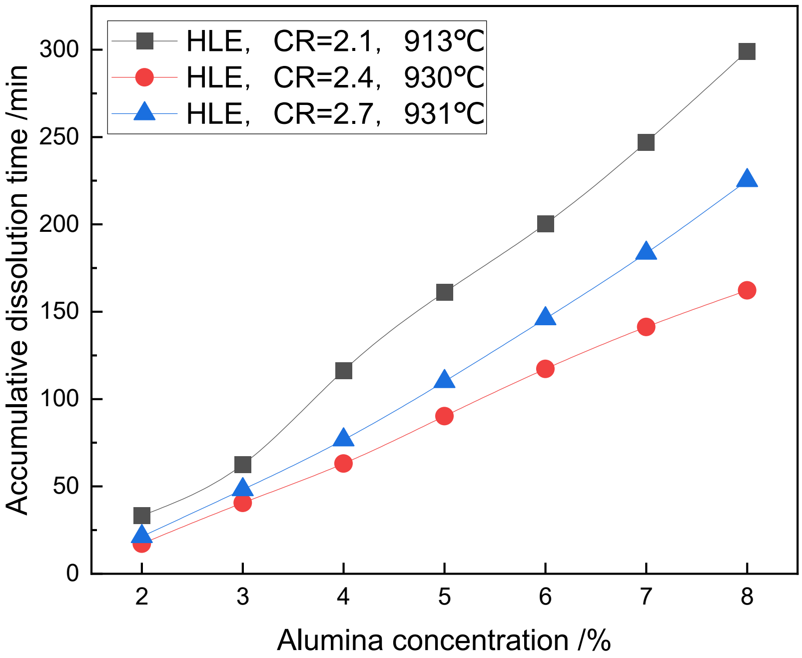

Figure 6 Comparison of the accumulative dissolution time of the secondary alumina in HLEs with different cryolite ratio.

Pascal Lavoie et al. presented some general fundamental rules in their review papers [4]. However, as discussed in Xiangwen Wang's papers, there were many discrepancies and controversies on dissolution behavior of alumina in literatures [3]. The studies on alumina dissolution will continue to be an interesting research field because of its complexity of fundamental and importance for high amperage reduction cells.

In this study, it was confirmed that the dissolution behavior observed has relationship with bath compositions. In modern aluminum reduction cells, SEs with CR = 2.1-2.3 are widely used. In some Chinese smelter, HPEs with CR=2.6-2.7 are typical compositions. From this study, SE with CR = 2.1 and HPE with CR = 2.7 have close liquidus temperatures, correspondingly close test temperatures. Compared to SE with CR = 2.1, HPE with CR = 2.7 exhibits slightly faster dissolution rate. This indicates that alumina dissolution should not be a problem for cells using HPE. However, according to authors' observation, a heavy alumina sludge was always detected in some industrial cells using HPE. After checking the industrial electrolyte of these cells, heavy carbon dust was found in it. The concentration of carbon dust is in the range of 0.6-1 %. The alumina dissolution method adopted in this study was used to observe secondary alumina dissolution behavior in the industrial electrolyte of HPE with heavy carbon dust. After melting, a viscous layer was observed on the surface of the ambiguous HPE melt. After adding alumina, an alumina agglomeration was formed on the surface of the melt as expected. But the agglomeration floated on the melt surface for over twenty minutes and did not sink to the crucible bottom until stirred with a metal rod, which was quite different from that of clean melt.

4. Conclusions

The dissolution behavior of the secondary alumina was investigated in three types of aluminum electrolytes. These aluminum electrolytes are widely used in Chinese aluminum smelters. Comparative study confirmed that electrolyte containing high content of lithium fluoride exhibited the poorest dissolution ability of alumina because of its lowest liquidus temperature and lowest alumina saturation concentration. Electrolyte containing high content of potassium fluoride exhibited similar dissolution behavior of alumina with that of simple electrolyte. However, heavy carbon dust has great impact on alumina dissolution and deteriorate the alumina dissolution by forming agglomerates. Superheat of bath lower than 5 °C has negative impact on alumina dissolution.

5. Acknowledgments

The authors would like to express their gratitude for the financial support provided by the National Natural Science Foundation of China (Grant Nos. 51574070, 51534005).

6. References

1. National Bureau of Statistics of China. http://www.stats.gov.cn/.
2. Wenmin Gu, The evolution of lithium and potassium in electrolyte in the aluminum smelter, *The 9th Symposium of Non-ferrous Industrial Technology Development in the Middle West of China*, Lanzhou, China, 21 – 22 September 2016, 668-671.
3. Xiangwen Wang, Alumina dissolution in aluminum smelting electrolyte, *Light Metals* 2009, 383-388.
4. Pascal Lavoie, Mark P. Taylor, James B. Metson, A Review of alumina feeding and dissolution factors in aluminum reduction cells, *Metallurgical and Materials Transactions B*, Volume 47B, August 2016, 2690-2695, https://doi.org/10.1007/s11663-016-0680-3.
5. Egil Skybakmoen, Asbjørn Solheim, Åsmund Sterten, Alumina solubility in molten salt systems of interest for aluminum electrolysis and related phase diagram data, *Metallurgical and Materials Transactions B*, 1997, Volume 28B, 81-86.
6. Asbjørn Solheim, Sverre Rolseth, Egil Skybakmoen, Lisbet Støen, Åsmund Sterten and Trond Støre, Liquidus temperatures for primary crystallization of cryolite in molten salt systems of interest for aluminum electrolysis, *Metallurgical and Materials Transactions B*, Volume 27B, October 1996, 739-744, https://doi.org/10.1007/BF02915602.