Issues of spent carbon potlining processing

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Abstract

While producing one ton of primary aluminum metal, 25 ± 15 kg of spent potlining (SPL) is generated with high content of carbon, fluorine compounds, including fluorite and cryolite, alumina, various cyanides, aluminium nitride and carbide, etc. Those wastes are specified as high hazard class and their disposal without prior neutralization is prohibited in some countries. Spent potlining can be processed into recycled cryolite and carbon material providing certain process improvement for fabrication of Portland cement and possessing high calorific value. The paper specifies individual steps of the process and potential of its implementation in units of cryolite regeneration from carbon dust. It was demonstrated that under new economic conditions it is possible to reduce operation costs for SPL processing and provide the required quality of recycled cryolite.

Keywords: Spent carbon potlining; cyanides; recycled cryolite; carbon-bearing material.

1. Introduction

With world annual production of more than 53 million tons of primary aluminum, more than 1 Mt of spent potlining (SPL) is generated, i.e., about 25 kg of toxic waste per ton of Al [1]. SPL was originally classified as industrial waste or mining waste that did not prevent its recovery or disposal. In the early 1980's Aluminum Association (AA) classified SPL as hazardous waste, based on the fact that SPL contains simple and complex cyanides, nitrides, carbides, soluble fluorides, and that after its interaction with water the medium becomes alkaline,. In 1988, US Environmental Protection Agency classified SPL as hazardous waste of class KO 88. In Canada, it was classified as special waste. Some difficulties appeared in connection with disposal or use of non-neutralized lining in cement and steel industry. Introduction of new regulations has led to the fact that SPL must be neutralized prior to delivery to a third party [2]. Right now, governmental regulations and high environmental payments for waste disposal are the main force for neutralization and processing of SPL.

In the former Soviet Union, thanks to a government program, the problem of SPL processing into secondary cryolite and carbon-containing fuel in the 1980's and 1990's was solved at the state level. Unfortunately, due to the collapse of economic ties, railroad rates increase, reduction in demand for secondary cryolite and a number of problems in processing technology, this program was halted.

Right now, concentration of the largest aluminum smelters in the Siberian region of Russia, substantial increase in the cost of fluorite concentrate and cryolite produced from it, the increase of environmental payments for SPL disposal and other reasons transformed secondary cryolite and other fluorides production into economically attractive process.

2. Processing options for spent potlining

In the USSR the following methods were already developed in 1960's and industrially implemented in 1970's to 1980's:

- Hydro-chemical method of spent potlining processing into secondary cryolite [2, 3, 4, 5],
- Thermal method using SPL in steel industry as flux addition [6, 7, 8].

Rio Tinto Alcan developed SPL digestion method comprising autoclave processing of all fluorine content into insoluble fluorite, cyanide destruction at a temperature of 180 °C and subsequent disposal [9].

Majority of proposed processes are based on hydro-chemical method consisting of conventional chain of process steps: crushing and milling, alkaline digestion followed by precipitation of the main component, thickening, filtration and drying. Figure 1 represents such generic flow diagram of SPL processing into secondary cryolite [10].

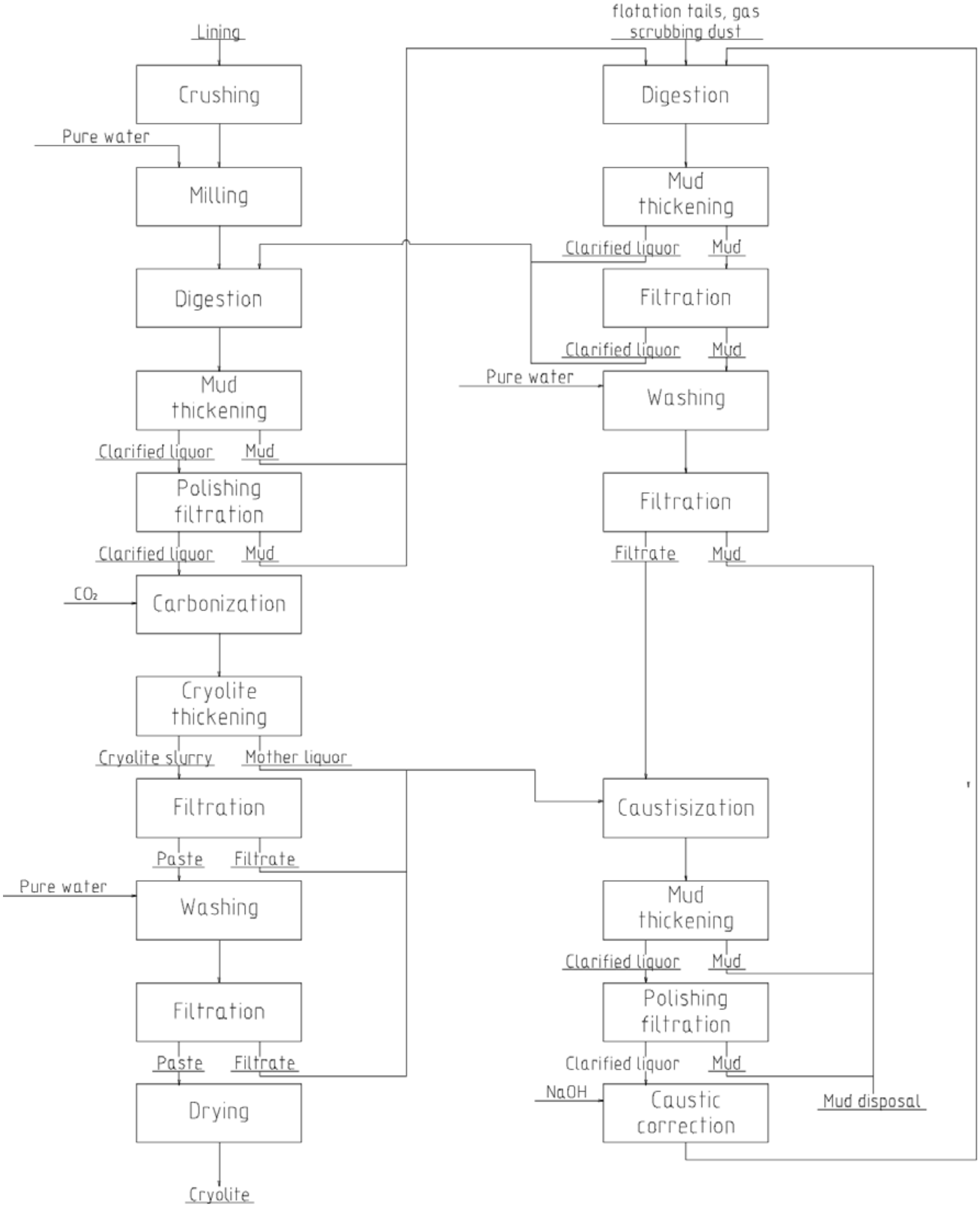

Figure 1. Flow diagram of SPL processing into cryolite [10].

3. Optimisation of the spent potlining processing parameters

After de-lining aluminium cells part of refractories (fire clay filling and bricks) enters into the first (carbon) layer, leading to the increase in SiO_2 content in the lining to be processed and impacts processes on digestion and desilication, as well as the composition of the produced cryolite and carbon material. Due to this the studies were conducted to produce secondary cryolite from SPL containing 10 % and 20 % of fire clay (chamotte). Chemical analysis of the samples is presented in Table 1.

Table 1. Chemical analysis of the samples.

Sample composition	Main components, mass %										
	F	Al_2O_3	Na^+	K^+	SO_3 (total)	SiO_2	CaO	Fe_2O_3 total	P_2O_5	LOI	Incl. C
Potlining	12.3	8.6	15.6	1.3	0.8	1.7	5.1	0.9	0.012	44.6	47.0
Pot fire clay	1.5	42.5	0.1	0.1	0.1	50	1.4	0.1	0.036	0.80	N/A
90 mass % lining + 10 mass. % pot fire clay	11.22	11.99	14.05	1.18	0.73	6.53	4.73	0.82	0.014	40.2	N/A
80 mass % lining + 20 mass % pot fire clay	10.14	15.38	12.5	1.06	0.66	11.36	4.36	0.74	0.017	35.8	N/A

Based on the experience and data of caustic concentration impact on fluorine and alumina solubility (Figure 2), digestion was conducted using caustic liquor with different concentrations Na_2O caustic.

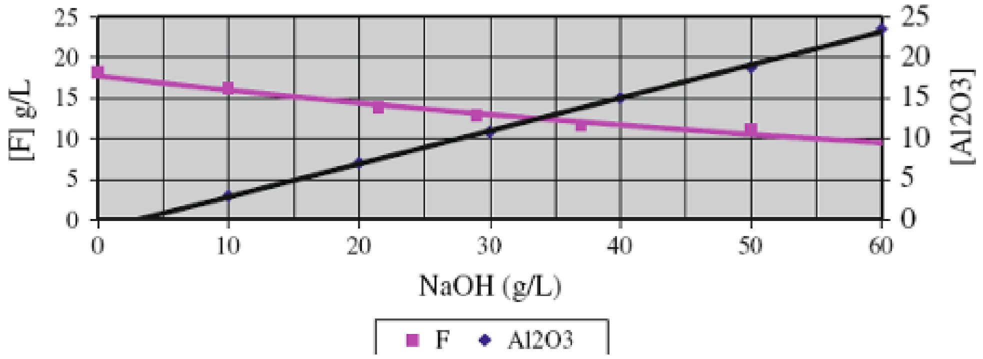

Figure 2. Solubility of NaF versus Al_2O_3 concentration in liquor [9].

The results of digestion of the samples are presented in Table 2. As is evident from Table 2, SiO_2 content in samples, varying in wide range from 1.7 to 11.36 mass %, has minor impact on SiO_2 transition in liquor that varies within 0.2 – 0.6 kg/m^3. The target value of SiO_2 content in clarified solution is not reached, which will affect the quality of secondary cryolite. For further silica reduction, desilication of clarified liquor with additives is required. Considering low flow of the produced secondary cryolite and its mixing with regenerative cryolite this parameter can be neglected as being non critical.

X-Ray phase analysis of mud after digestion demonstrated that for all studied conditions complete transition of sodium fluorite and cryolite into solution occurs. Fluorine losses with solid fraction are conditioned by fluorite in samples (CaF_2), insoluble in water and alkali under given conditions.

As is seen from the flow diagram the main input material flows for secondary cryolite generation are:

- Lining,
- Caustic,
- Carbon dioxide.

Table 2. Results of spent potlining digestion with fire clay addition.

# exp.	Pot fire clay, %	Liquor analysis, kg/m^3						
		F	SiO_2	Fe_2O_3	Al_2O_3	Na+	CO_2	P_2O_5
1	0	19.5	**0.43**	0.0023	5.5	27.9	-	-
2	10	19.1	**0.34**	0.0028	4.9	24.1	0.26	0.0006
3	20	18.0	**0.59**	0.0022	4.5	22.5	-	-
4	0	15.3	**0.52**	0.0038	4.0	23.8	-	-
5	10	19.0	**0.53**	0.0036	4.8	23.0	0.20	0.0006
6	20	17.6	**0.49**	0.0039	4.1	21.8	-	-
7	20	16.5	**0.24**	0.0020	4.1	19.2	-	-
8	20	16.4	**0.36**	0.0036	4.1	19.1	0.16	0.0006

For determining of impact of high sulfate content in mud water a set of experiments was conducted with industrial mud water under the following conditions:

- Temperature = 80 °C,
- Mixing procedure: in clarified liquor the calculated amount of aluminate liquor was slowly added, followed by two equal portions of the neutralization liquor with several minutes interval,
- Residence time in mixing reactor after addition of aluminate and bicarbonate liquors was 2 hours,
- Moderate mixing.

After digestion the slurry of secondary cryolite was filtered on Bucher funnel. Filtered cryolite was reslurried by hot water of 80 – 90 °C to liquid-to-solid ratio of 2 to 1 (by mass), held while stirring during 10 minutes and filtered again. In washed and filtered cryolite the residue weight, moisture, chemical analysis (including F, S, Al, Na), phase analysis and grain size were determined. In mother liquor the Na was determined in a form of caustic soda, sodium carbonate and bicarbonate, Al, F, S (total). The results of cryolite digestion under laboratory conditions are presented in Figure 3 and Table 4.

Table 3 –Analysis of cryolite produced using industrial mud water.

Experiment	Cryolite chemical analysis, mass %								Particle average diameter, µm
	F	Na	SiO_2	Al	SO_3 total	Fe_2O_3	LOI	Criolite Ratio	
1	54.1	25.1	0.53	13.6	1.3	0.28	22.2	2.20	16.63
2	56.5	22.6	0.41	15.1	1.1	0.15	22.7	1.94	15.08
3	54.6	22.3	0.11	16.3	0.9	0.08	25.0	1.98	20.53
GOST requirements	> 54.0	> 22.0	< 0.9	< 19.0	< 1.0	< 0.1	Not specified	> 1.5	Not specified

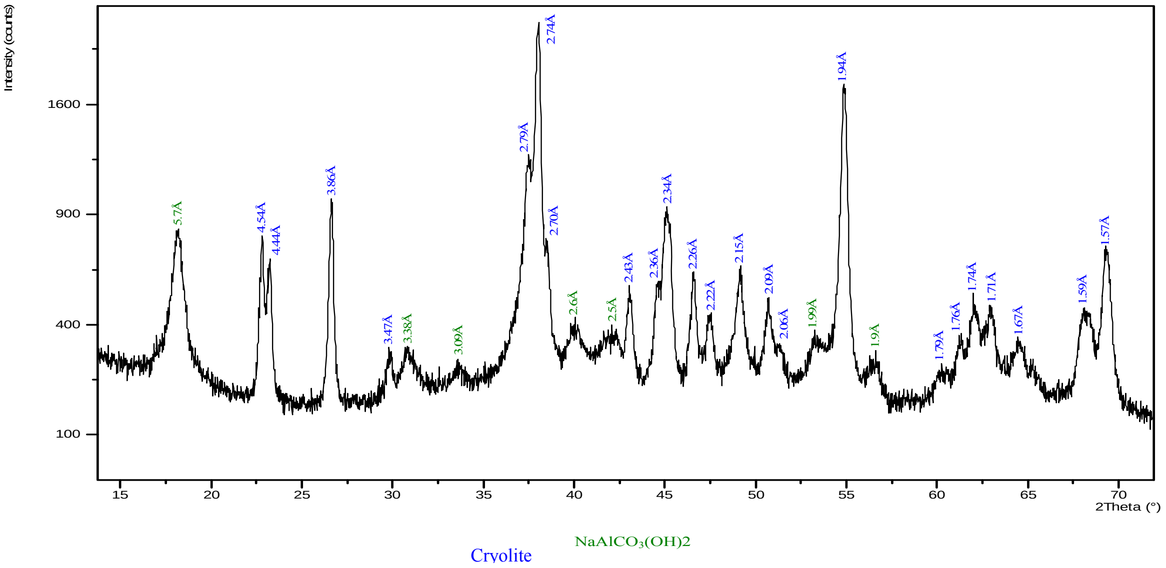

Figure 3. Cryolite X-ray pattern after neutralization with mud water.

The mud produced after digestion was considered as flux addition and as solid fuel. In specialized carbon laboratory the analysis of two carbon samples was made:

- Mud-free fire clay,
- Mud with 20 % addition of fire clay.

The results are summarized in Table 5. Carbon material produced after SPL processing can be characterized as low-calorific coal. For example, the coal supplied to Achinsk refinery (from different Kuzbass coal mines has calorific value from 24.70 MJ/kg to 25.54 MJ/kg, and brown coal from Berezovskoye mine from 15.07 MJ/kg to 16.33 MJ/kg.

In the initial SPL sample volatile content was 1.6 %. After digestion the volatiles in carbon material were reduced to below 1 %.

Table 5. Analysis of 2 samples of spent potlining digested at specified conditions.

No	Parameter	Unit	Sample*	
			2 (free of fire clay)	3 (with 20 % fire clay)
1	Total Moisture	%	0.4	0.4
2	Moisture (AD)	%	0.4	0.4
3	Slag melting point	°C	815	850
Dry ashless				
4	Gross calorific value	MJ/kg	33.11	31.11
For product mass				
5	Ash Content	%	27.70	46.08
6	Volatile Matter	%	0.77	1.00
7	Total Sulfur	%	0.11	0.09
9	Gross heat value	MJ/kg	23.94	16.77
11	Net heat value	MJ/kg	23.92	16.74
12	Carbon	%	71.88	52.84
13	Hydrogen	%	0.12	0.17
14	Nitrogen	%	0.00	0.00

The specifics of the produced carbon material are high ash content and relatively high fluorine content (2 - 3 mass %). Therefore ash has a low melting point (≈ 850 °C), which requires adjustment of the combustion mode for the use of carbon material as process fuel. Due to the insignificant amount of carbon material (≈ 10 000 tons per year) it is advisable to use it as flux addition in cement production, allowing to reduce by 30 – 50 °C clinker formation regime and amount NO_x emissions.

4. Conclusions

- X-Ray phase analysis demonstrated that in all cases cryolite was produced. Traces of chiolite ($5NaF \times 3AlF_3$) are not detected. In 2 samples insignificant amount (≈ 2 - 3 %) of polymorphous nordstrandite (γ-$Al(OH)_3$) is determined;
- Cryolite samples differ in SiO_2 content by ≈ 4.5 times, from 0.11 to 0.53 mass %, but even with the highest silica content were significantly below the limit value of GOST (Russian Standard);
- Calculation of cryolite ratio by chemical analysis demonstrated variation from 1.94 to 2.2.
- Grain size measurement of the produced secondary cryolite demonstrated that an average particle size varies from 15 to 20 micrometers.

5. Acknowledgements

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