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Determination of Metal Elements in Red Mud Using Inductively Coupled Plasma-Atomic Emission Spectrometry

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Herein, two kinds of red mud from Sintering and Bayer processes in Henan Branch of Chinese Aluminum Company were characterized quantitatively and qualitatively using the techniques of inductively coupled plasma-atomic emission spectrometry (ICP-AES). Forty six and forty seven kinds of metal elements were found and measured in red mud from Bayer and Sintering process respectively, supporting the recovery value of several metals such as Fe, Ga, Sc and U, *etc*.

Keywords: ICP-AES, Metal element, Red mud, Determination.

INTRODUCTION

Red mud is a solid waste residue from alumina manufacturing. It is reported that about 1 to 2 tons red mud will be generated from the production of 1 ton alumina[1]. Every year, about 90 million tons red mud is discharged worldwide and approximate 1/3 of them come from China[2,3]. These red muds are always stocked up on land. However, red mud is a kind of strong alkaline waste with average pH of 10-13 of its lixivium. The large emission of red mud has caused serious pollutions to soil, water and even air. So the treatment and disposal of red mud has become a major problem for alumina manufacturing and efficient approaches are highly desired.

In the past several decades, numerous works have been carried out to develop an economic method for the utilization of red mud. Pulford, Regina and Zhao *et al*. took red mud as original material to prepare adsorbents for the removal of heavy metal ions, dyes, phosphate, nitrate and fluoride[4-6]. Red mud was also proved to be an efficient supporter of Co catalysts for phenol oxidation[7]. Because of high contents of metal elements like iron, aluminum, titanium, cadmium, scandium, gallium, uranium *etc*, red mud commonly used as raw material for metal extraction[3,8,9]. These works suggested red mud as a useful material in various industries. However, the vital problem for the use of red mud is the comprehensive analysis on its components included the contents and the existing forms. Though many works have been reported on determinations of metals like iron, aluminum, titanium, silicon, calcium, sodium and scandium, there are few researches on other metal elements like caesium, gallium, uranium *etc*. Especially, rare works have reported all metal species and their contents in red mud.

There are two processes for alumina production, namely Bayer process and Sintering process, resulting two kinds of red mud with different properties. In the present work, both kinds of domestic red mud from Henan Branch of Chinese Aluminum Company were characterized quantitatively and qualitatively. Almost all metal elements existed in both red mud were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) technique, as well as some metals were measured with atomic absorption spectroscopy (AAS) and titration methods as comparisons.

EXPERIMENTAL

Sintering and Bayer red muds were supplied by Henan Branch of Chinese Aluminum Company. The sample were first settled in a cool ventilated place to dry naturally and then were pestled over and over again until all samples could be sifted through 200 mesh (d = 0.074 mm) sieve. All atomic spectroscopy standard solutions for ICP-AES (1000 mg/L) were furnished from Alfa and the other reagents were analytical grade and were used as received.

A typical pretreatment process for red mud sample was as following: wet 0.5000 g red mud with 2-3 mL high purity water in a 50 mL Teflon digestion tank, followed by adding 10 mL hydrochloric acid; subsequently, the slurry was then kept at 100 °C until the volume decreased to 2-3 mL. After being cooled to room temperature, 5 mL of hydrofluoric acid was added and the tank was then sealed and kept at 100 °C for 60 min, as following the slurry was condensed to 2 mL; after 8 mL nitric acid and 2 mL perchloric acid being added, the slurry was kept at 150 °C until no white smoke exuded. The final sample was diluted by high purity water to 100 mL, with 1-2 mL nitric acid as stabilizer. It is noted that all experiments performances should conducted in fume cupboard. The quantitative determinations of metal elements were performed on Optima 2100DV ICP-AES (USA, PekinElmer) with operating parameter as: radio-frequency power, 1300 W; sample amount, 1.5 mL/min; carrier gas flow rate, 1.2 L/min; auxiliary gas flow rate, 0.2 L/min; atomizer gas flow rate, 0.80 L/min; repetition, 3 times; reading delay, 60 s. Two kinds of multielement standards were prepared with atomic spectroscopy standard solutions. One is the elements in 5 % HNO_3 consisted of Al, Ca, Fe, Sr, Mg, Mn, Na, Y, Cs, Cu, La, Sc, Ce, Ba, U, K, Ni, Yb, Li, Be, Pr, Dy, Tm, Th, Hg, Co, V, Gd, Lu, Cd, Rb, In, Er, Ho, Tb, Sm and Nd; and, the other is the elements in 5 % HCl/tr. HF involving Ti, Nb, Zr, Ga, Cr, Ru, Rh, Pt, Hf, Au, Pd, Os and Ta.

RESULTS AND DISCUSSION

The qualitative scanning of metal elements was first conducted. There are 50 and 48 kinds of metal elements that were found with calibration intensities given as positive values in Bayer and Sintering red mud, respectively. The positive intensities reflected the appearances of elements to some extent. Thus, the corresponding elements were determined quantitatively and results were shown in Table-1. 46 and 47 kinds of elements were verified existing in Bayer and Sintering red mud, respectively. It was found that both red mud contained large amounts of Ca, Al, Fe, Ti, Cs and Mg. The contents of Ga amount to 0.21 and 0.18 % in Bayer and Sintering red mud, respectively, which are approach to other Ga minerals. For example, the content of Ga in germanite, a kind of Ga-enriched mineral, is always 0.1-0.8 %. Contents of U are also reached to the grade of common U ore, obtained as 0.066 and 0.057 % in Bayer and Sintering red mud respectively. In addition, both red muds also consisted of considerable noble metals (Pt, Rh, Ru, Pd and Os *etc*.) and rare earth metals (Sc, Y and La *etc*.).

TABLE-1
CONTENTS OF VARIOUS METALS IN BAYER AND SINTERING RED MUDS

Analyte	λ(nm)	Percentage (%)		Analyte	λ(nm)	Percentage (%)	
		Bayer	Sintering			Bayer	Sintering
Ca	317.933	7.55	27.32	Ba	233.527	0.015	0.04138
Al	396.153	10.16	2.64	Os	228.226	0.01492	0.003838
Fe	238.204	9.062	8.212	Sc	361.383	0.01366	0.01278
Na	589.592	3	0.9	Rb	780.023	0.01218	0.008001
Ti	334.94	2.432	2.529	Th	283.73	0.009462	0.007588
Cs	455.531	2.087	1.93	Au	267.595	0.006875	0.00505
K	766.49	1.506	0.5938	Pd	340.458	0.006062	0.00485
Mg	285.213	1.134	1.783	Yb	328.937	0.005	0.005
Cu	327.393	0.2125	0.2125	Co	228.616	0.003862	0.00365
Ga	417.206	0.2104	0.1845	Ce	413.764	0.003212	0.007738
Hf	277.336	0.178	0.1679	Dy	353.17	0.002988	0.003025
Ru	240.272	0.1538	0.2281	La	398.852	0.001875	0.006125
Sr	407.771	0.1025	0.1338	Ho	345.6	0.00136	0.00162
Nb	309.418	0.0925	0.09	Sm	359.26	0.001346	0.00124
Cr	267.716	0.08238	0.09875	Pr	390.844	0.0012	0.001725
Zr	343.823	0.07218	0.04388	Nd	406.109	0.001075	0.001075
U	385.958	0.0633	0.05702	Be	313.107	0.000875	0.000625
Cd	228.802	0.05662	0.05662	Lu	261.542	0.00065	0.00065
Y	371.029	0.049	0.0495	Er	369.265	0.0005	0.000175
Ni	231.604	0.045	0.1125	Gd	376.839	0.0002749	0.000475
Hg	253.652	0.04049	0.0306	Tm	313.126	-	0.001062
Mn	257.61	0.03488	0.0435	Tb	350.917	-	-
Rh	343.489	0.03315	0.0262	Eu	381.967	-	-
Pt	265.945	0.0316	0.01828	In	230.606	-	-
Li	670.784	0.02594	0.03424	Ta	226.23	-	-
V	292.464	0.02395	0.02416	W	207.912	-	-

TABLE-2
STANDARD RECOVERY RATE FOR SEVERAL METALS USING ICP-AES

Analyte	Bayer				Sintering			
	Measured (mg/L)	Addition (mg/L)	Total (mg/L)	Recovery rate (%)	Measured (mg/L)	Addition (mg/L)	Total (mg/L)	Recovery rate (%)
Ca	377.5	500	907.5	106	1366	1000	2276	91
Al	508	500	1023	103	132	200	346	107
Fe	453.1	500	953.1	100	410.6	500	925.6	103
Na	150	100	252	102	45	100	153	108
K	75.3	100	177.3	102	29.69	100	132.69	103
Mg	56.7	100	156.7	100	89.15	100	197.15	108

TABLE-3
COMPARISONS AMONG ICP-AES, AAS AND EDTA METHODS FOR SEVERAL METALS IN BAYER AND SINTERING RED MUDS

Analyte	Bayer (%)			Sintering (%)		
	ICP-AES	AAS*	EDTA**	ICP-AES	AAS*	EDTA**
Ca	7.55	7.91	8.279	27.32	33.55	30
Al	10.16	-	8.721	2.64	-	2.27
Fe	9.062	8.685	10.09	8.212	8.48	8.833
Na	3	2.916	-	0.9	0.937	-
K	1.506	1.731	-	0.5938	0.6663	-
Mg	1.134	1.424	1.325	1.783	1.78	1.92

To determine the accuracy of ICP-AES results, standard addition recovery experiments were conducted with Ca, Al, Fe, Na, K and Mg, as well as these elements were examined by atomic absorption spectroscopy (AAS) and titrimetric method with ethylenediaminetetraacetic acid disodium salt (EDTA). Tables 2 and 3 further confirmed the feasible of determinations of metal elements by using ICP-AES technique.

Conclusion

Both kinds red mud of Bayer and Sintering from Henan Branch of Chinese Aluminum Company were carefully analyzed by ICP-AES, comparing with AAS and EDTA methods. Forty six and forty seven kinds of metal elements were measured quantitatively to discuss the feasibility of recovering useful metals. The present work support an ICP-AES method for determination of metal elements in red mud, thus permit us evaluate the recoveries of metals. It is of great importance for the comprehensive utilization of red mud.

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