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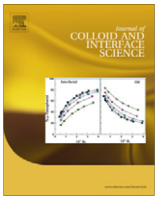

Surface electrochemical properties of red mud (bauxite residue): Zeta potential and surface charge density

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ABSTRACT

The surface electrochemical properties of red mud (bauxite residue) from different alumina refineries in Australia and China were studied by electrophoresis and measuring surface charge density obtained from acid/base potentiometric titrations. The electrophoretic properties were measured from zeta potentials obtained in the presence of 0.01 and 0.001 M KNO_3 over a wide pH range (3.5–10) by titration. The isoelectric point (IEP) values were found to vary from 6.35 to 8.70 for the red mud samples. Further investigation into the surface charge density of one sample (RRM) by acid/base potentiometric titration showed similar results for pH_{PZC} with pH_{IEP} obtained from electrokinetic measurements. The pH_{IEP} determined from zeta potential measurements can be used as a characteristic property of red mud. The minerals contained in red mud contributed to the different values of pH_{IEP} of samples obtained from different refineries. Different relationships of pH_{IEP} with Al/Fe and Al/Si ratios (molar basis) were also found for different red mud samples.

1. Introduction

The management of red mud bauxite residue is a serious and extremely challenging waste problem that is a major concern to alumina refineries all over the world. Approximately 90 million tonnes of this alkaline and saline waste are generated globally every year [1]. Adequate treatment and proper disposal are essential due to its corrosive properties and related harmful effects on the environment [2]. Because of its corrosive nature land-based disposal of red mud is prohibited in most jurisdictions unless contained in specially designed landfills that are not available in many countries. Recent research has focused on the conversion of red mud into less corrosive forms and to enhance its capacity as adsorbent/catalysts for the removal of heavy metals and organic pollutants [3–6]. Investigations into red mud samples related to their efficiency for removal of pollutants have also been made, including their basic physical, chemical and mineralogical properties [2,7–11]. However, few studies focus on the surface chemical properties of red mud, which is the interface for sorption reactions [12–14].

Red mud is a heterogeneous mixture of fine-grained solids, mainly consisting of haematite, gibbsite, quartz, titanium oxide, carbonates and desilication products (cancrinite, sodalite, etc.). Inter- and intra-particle behaviour in the presence of water (and the inherent dissolved salts) is critically dependent on the surface charge of the constituent particles. The physical and chemical behaviour of red mud materials, such as rheology, aggregation and coagulation, surface hydration, ion exchange capacity, pH buffering capacity, adsorption capacity and redox behaviour, is highly dependent on the surface charge properties of individual particles [11]. To understand the behaviour of red mud as an adsorbent or catalyst, it is necessary to characterise such surface properties as the density of ionisable sites and their tendency to ionise [13].

Surface charge density (σ) describes the net uptake of protons per unit of surface area and can be determined from potentiometric titration curves. Alternatively, electrokinetics can be applied as it is practical to find a measure of the extent to which electrostatic interaction contributes to the stability of dispersion [15]. Electrophoresis of charged particles is easy to determine by convenient apparatus from which the zeta potential (ζ) is computed [15]. In this study, we determined the zeta potential and surface charge density of red mud suspensions to characterise the surface chemical properties of red mud samples obtained from different refineries that vary in bauxite ore sources and refining processes employed.

2. Materials

Red mud samples with different origins were collected from CHALCO (Aluminium Corporation of China Limited) and Rio Tinto Alcan Yarwun refinery, Australia. The red mud samples were air

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dried, crushed and analysed by X-ray fluorescence spectroscopy (XRF, PANalytical Axios Advanced wavelength dispersive XRF) and X-ray diffraction (XRD, Empyrean XRD PANalytical instruments, Netherlands) for chemical and mineral composition. Surface area was determined by a Micrometrics Tristar 3000 using the BET (Brunauer, Emmett, and Teller) method. The pertinent properties of red mud samples are summarised in Table 1.

3. Methods

3.1. Theory

In colloid systems, the surface charge structure of solids is well described by the double layer theory [22–24]. For a negative charged surface, the counter ions stay close to the surface as the inner or Stern layer. With increasing distance from the charged surface, there will be diffuse layer containing both anions and cations until it reaches the composition of the bulk solution. The diffuse layer is positively charged, also called slipping plane, which the zeta potential measures [25]. Zeta potential can provide valuable information about the structure and properties of the double layer, even though the exact location of the slip structure cannot be ascertained.

Natural particles develop surface charge by three mechanisms [25,26]: (i) structural substitution, σ_0; (ii) adsorption of protons, σ_H; (iii) adsorption of ions, q_+, or q_-. Δq (q is the total relative adsorption of cation or anion) can be described in molecular terms in three subcategories:

$$\Delta q \equiv \sigma_{IS} + \sigma_{OS} + \sigma_d \tag{1}$$

where σ_{IS}, σ_{OS} and σ_d refer to the net charge of ions adsorbed in inner-sphere surface complexes, outer-sphere surface complexes and the diffuse layer, respectively [26]. The pH at which the net total particle charge is zero is called the point of zero charge (PZC), which is one of the most important parameters used to describe variable charge surfaces [27]. In the absence of specific adsorption (σ_{IS}, σ_{OS}) in the system, the surface charge is dominated by structural charge (if any) and variable charge derived from adsorption of protons. The charge balance in this case would be $\sigma_0 + \sigma_H + \sigma_d = 0$. At the pH_{PZC}, the net total particle charge is equal to zero, which means $\sigma_p = \sigma_0 + \sigma_H + \sigma_{IS} + \sigma_{OS} = 0$, for absence of σ_{IS}, σ_{OS}, $\sigma_p = \sigma_0 + \sigma_H = 0$, which is balanced by σ_d. Therefore, in systems without ($\sigma_{IS} + \sigma_{OS}$),

Table 1
Pertinent properties of red mud samples.

Sample	SDBE	GXBE	RRM	NRM	SDSJ	HNZZ-1	HNZZ-2	SMX	PZC/IEP	Range
Origin	China	China	Australia	Australia	China	China	China	China	–	
Refining process	B[a]	B	B	B	S[b]	C[c]	C	C	–	
Year of sampling	2009	2009	2009	2009	2009	2006	2006		–	
Surface area (m^2/g)	13.06	6.92	24.25	22.97	22.37	7.43	9.40	11.44	–	
Measured IEP	7.11	8.70	6.83	6.35	7.74	8.59	6.67	8.18	–	
Chemical composition (wt%)										
SiO_2	24.36	9.07	13.88	11.12	12.66	14.8	18.33	17.11	2.0 [16]	
TiO_2	1.58	6.78	6.84	5.32	2.46	4.54	4.39	6.26	5.6 [17]	5.1–6.4[17]
Al_2O_3	19.57	17.9	22.53	19.77	11.79	21.5	11.62	21.24	8.37[d]	8.5–9.0[17]
Fe_2O_3	31.48	34.28	34.48	22.99	9.37	6.45	10.54	8.27	8.03[d]	
CaO	2.35	12.19	1.83	2.66	26.95	26.06	33.45	21.77	–	
Na_2O	8.67	4.42	9.41	16.52	5.33	3.54	3.42	6.77	–	
Mineralogical composition										
Quartz (SiO_2)	+ +[e]		+[f]	+		+	+		2.6 [18]	2.3–2.8
Haematite (Fe_2O_3)	+ +	+ + +[g]	+ + +	+ + +		+		+	7.8 [17]	6.0–9.1
Magnetite (Fe_3O_4)					+		+		6.5 [17]	5.7–6.8
Geothite,aluminian ($(Fe_{0.93}Al_{0.07})O(OH)$)	+ +								–	
Geothite (FeO(OH))		+							7.8 [17]	6.6–8.6
Calcite ($CaCO_3$)	+	+	+	+	+ + +	+ +	+ +	+	8.2 [19]	
Aragonite ($CaCO_3$)					+ +				<6 if any[20]	
Perovskite ($CaTiO_3$)		+			+		+ +		8.1 [21]	
Sodalite ($Na_{7.6–8}(Al_6Si_6O_{24})(CO_3)_{0.93}Cl_{0–2}(H_2O)_{0–0.93}$)	+ +		+ +	+ +					NR[h]	
Cancrinite ($Na_{6.02–8}Ca_{0.4–1.52}(Al_6Si_6O_{24})(CO_3)_{0–1.46}(OH)_{0–2.04}(H_2O)_{0–6}$)		+ +				+ +		+ + +	NR	
Gibbsite ($Al(OH)_3$)	+	+							6.5 [17]	3.8–9.9
Boehmite (AlO(OH))			+ +	+ +					8.9 [17]	8.1–9.7
Diaspore (AlO(OH))		+							7.9 [17]	6.9–8.8
Bayerite ($Al(OH)_3$)						+			8.1 [18]	5.4–9.7
Nordstrandite ($Al(OH)_3$)						+			NR	
Katoite ($Ca_{2.93}Al_{1.97}(Si_{0.64}O_{2.56})(OH)_{9.44}$)		+ + +				+ + +	+ +	+ + +	NR	
Anatase (TiO_2)			+	+					5.5 [17]	5.3–5.6
Rutile (TiO_2)			+	+					5.8 [17]	
Halite (NaCl)				+ +					–	–
Magnesite ($MgCO_3$)							+ + +		7.7 [18]	6.2–8.7

[a] B: Bayer process.
[b] S: Sintering process.
[c] C: Combined Bayer and sintering process.
[d] Determined in this study.
[e] + +: 10–30%.
[f] +: <10%.
[g] + + +: >30%.
[h] NR: not reported.