Chapter 8
Zeta Potential and Particle Size Characteristics of Red Mud Waste

B. Hanumantha Rao and N. Gangadhara Reddy

Abstract Neutralization is essential for high alkaline wastes like red mud for its effective utilization. As such, the process of neutralization involves treating the red mud with either chemicals or other waste materials. Among several factors that affect the efficiency of the treatment, surface charge characteristics and particle diameter parameters predominantly influence the performance of the neutralization. The present study focuses on examining the surface charge properties which include flocculation and dispersion and determining the particle size characteristics which include mean particle diameter under variable pH conditions. Surface charge properties are interpreted from zeta potential, ζ, measurements made on suspensions prepared with red mud waste at different pH values. The average particle diameter is obtained from the grain size analysis established on the same suspensions using the zeta potential analyser. Results indicate that the zeta potential increases with pH up to a certain pH value of 4 and then begin to fall with the further increase in pH. The zeta potential turned into negative (up to a maximum value of −48 mV) at pH value of 6.6, which denotes the point of zero charge for the red mud, from the initial positive (from a maximum of +41.8 mV) value. However, the value becomes stabilized when the pH is 10 and above. An average particle diameter of (a) 65–150 nm at pH of 3.96 and above 9.00, indicating a complete dispersed state of the grains, and (b) 1660 nm, 2176 nm and 1080 nm at pH of 1.15, PZC (i.e. pH of 6.6) and pH of 7.48, respectively, indicating likely agglomeration of the grains, was recorded with the change in pH of the suspension. The study finds that the waste possesses surface charge characteristics, which appear to be greatly influenced by the pH.

Keywords Surface charge properties • Zeta potential • Particle size • Effect of pH • Red mud • Flocculation • Dispersion • Adsorption

B. Hanumantha Rao (✉) • N. Gangadhara Reddy
School of Infrastructure, IIT Bhubaneswar, Khurda, 752050 Bhubaneswar, Odisha, India
e-mail: bhrao@iitbbs.ac.in; gn11@iitbbs.ac.in

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8.1 Introduction

8.1.1 Red Mud Waste

Most of the developing countries are lacking in adequate technology for sustainable treatment and utilization of solid wastes/by-products generated in huge quantity annually. The physical presence of any waste poses a threat to land, water and environment as it can pollute them in the due course of time. Thus, utilization of the waste, instead of disposing of it, becomes inevitable. Several studies demonstrate that wastes or by-products can be employed for gainful utilization, especially in civil and environmental applications, which could be able to consume bulk quantity of waste materials.

Among many industrial by-products, red mud waste (RMW) is a solid waste residue formed after the caustic digestion of bauxite ores during the production of alumina (Parekh and Goldberger 1976). The high alkalinity (i.e. pH range from 10.5 to 13) is due to the presence of excessive caustic soda (NaOH) content that is added during the extraction of alumina from bauxite ore by Bayer's process. For every tonne of alumina produced, the process can leave 0.8–2.5 tonnes of red mud, depending on the origin and composition of raw material used. It is estimated that approximately 120 million tonnes of red mud is generated per annum from several numbers of aluminium refinery plants across the globe, and about 14 million tonnes of it is produced in India (Power et al. 2011). The waste usually is disposed in the form of slurry, which contains about 15–40% solids (Li 1998). In the last century, many countries (viz. France, Great Britain, Jamaica, Japan, Italy, USA) dumped red mud waste slurry simply into the sea. The disposal of red mud waste into the sea generally had a limited impact on the marine environment and marine organisms due to residual alkaline and fine particle suspension in the sea environment (Agrawal et al. 2004; Power et al. 2011). On the other hand, red mud waste produced by the alumina plants located in non-coastal areas have a practice of disposing the waste into the confined impoundments. The impoundments basically are divided into three types: (a) lagooning, (b) dry stacking and (c) dry cake disposal. The various types of disposal systems being in practice across India are shown in Table 8.1.

In the lagooning system, slurry form of red mud containing about 15 to 40% solids is pumped in. However, this kind of system requires lining at the bottom that acts as a sealant, minimizing the liquor leakage to the underlying ground and groundwater. The simplest is a single layer of compacted clay that separates the residue from the original soil of the storage area (Power et al. 2011). Additional security can be achieved by the use of multiple layers, featuring impermeable plastic or geomembrane materials to form a seal between the residue and the supporting clay or other layer beneath. Dry stacking system is a little different from lagooning system and is termed as thickened tailing disposal system (Power et al. 2011). In this sort of practice, slurry of waste containing approximately 48 to 55% solids is allowed. Initially, a thin layer of red mud waste slurry is disposed of, and the excess water is allowed to evaporate or is dewatered before placing of the next

Table 8.1 A summary on red mud waste generation and disposal practices adopted by alumina industry in India

Name of the plant	Present generation of red mud waste (million tonnes/annum)	Disposal or dumping practices
NALCO, Damanjodi	2.70	A modified close cycle disposal system is used for wet disposal. The bottom of the pond is covered with impervious and semi pervious clay with base filters
BALCO, Korba	1.30	Uses modified close cycle disposal system for wet disposal. The dykes of the currently used pond have stone masonry and well protected with clay layers
Hindalco, Renukoot, Belgaum and Muri	2.64	Dry cake disposal
		Dry cake disposal
		Wet slurry or lagooning disposal
Vedanta, Lanjigarh	1.82	Wet disposal
Utkal, Rayagada	1.93	Wet disposal
MALCO, Mettur	Closed (since November 2008)	Wet disposal

Prasad et al. (1996), Mohapatra et al. (2000), and Samal et al. (2013)

layer of slurry (Cooling 1989). The last type of disposal system is dry cake disposal, which refers to the removal of water as much as possible from the residue to produce a dry cake with a solid's content of more than 65% weight prior to disposal. The dry cake disposal is not an economical disposal method because the dry cake is not pumpable, so it is generally transported into the disposal area by conveyors or trucks (Shah and Gararia 1995) and increases particle suspended matter in the nearby environment (Rai et al. 2012).

In the lagooning disposal system, the chances for contamination of land and water are quite high. The contamination is essentially due to high alkalinity of the waste. This kind of system can pose a serious threat to environment. A catastrophic embankment failure of the red mud impoundment at Ajka, Hungary, on 4 October 2010, is a best example for this kind of disposal system. Around ten people died in this incidence, and life all along the river region vanished due to spillage of about one million cubic metres of highly alkaline red mud (Ruyters et al. 2011). Similarly, another such incident occurred at Luoyang, Henan Province of China, on 8 August 2016, releasing about two million cubic metres of red mud. A village with a population of more than 300 was severely affected by this incident, and many farms and domestic animals died. These examples of mine waste containment failures have led to major concerns regarding the storage practices of red mud. The high alkalinity is mainly impeding the large-scale utilization of red mud waste. In connection with this, many of the researchers suggested neutralization of the red mud employing either commercially available chemical solutions or industrial solid waste products (Reddy and Rao 2016; Gore et al. 2016).

Red mud waste is typically red in colour because of the presence of oxides of iron, which is a dominant compound in the total mass. The waste composes of a heterogeneous mixture of fine-grained particles, mainly consisting of iron, silicon, titanium oxides, hydroxides and other products (Liu et al. 2013). Typical particle compositions of red mud waste are shown in Figs. 8.1a and 8.1b.

The particle size was reported as 90% of the particles are finer than 75 μm in size and majority of the particles are in silt to clay size range, relatively with high specific surface area (13–50 m^2/g). The specific gravity of solids found to vary between the range from 2.7 to 3.3 (Parekh and Goldberger 1976; Kehagia 2010; Gräfe et al. 2011; Snars and Gilkes 2009). The combination of the heterogeneous particle size, chemical compositions, high specific gravity of solids and specific surface area makes the waste difficult to handle and utilize. Depending upon the origin, composition of the bauxite ore and type of alumina extraction method, the properties of the red mud vary widely from place to place and refinery to refinery (Parekh and Goldberger 1976; Bhatnagar et al. 2011). Clay-like minerals, which are quite common in conventional soils and responsible for inducing surface charge characteristics, however, are absent in the waste. Even then, the waste particles still exhibits surface charge characteristics similar to that of conventional clays. This behaviour may be due to constituent particle gradation, pore sizes and electrically charged properties of the hydroxysodalite, goethite and hematite minerals present in the red mud (Newson et al. 2006).

8.1.2 Zeta Potential

Zeta potential, ζ, is the electric potential in the interfacial double layer at the location of the slipping plane relative to a point in the bulk fluid away from the interface (refer to Fig. 8.2a). In other words, zeta potential is the potential difference between the dispersion medium and colloidal particle. Zeta potential is usually measured to know the behaviour of particle's surface charge characteristics which include flocculation and dispersion (refer to Fig. 8.2b).

Zeta potential is nothing but refers to strength of the interparticle repulsive force and is often used to define the state of slurry: flocculated or dispersed. Zeta potential is an intrinsic property of a material in liquid suspension, and the knowledge of it gives an insight into the strength of electrical double layer (EDL) and the stability of a colloidal system. Usually, stability of suspensions directly depends on the zeta potential of particles (Avadiar et al. 2014; Au and Leong 2015). The pH has a great influence on the zeta potential, and it can alter the sign of electric surface charge on the particle surfaces under extreme pH conditions. The colloidal behaviour of material suspension changes with the change in particle size due to change in their surface charge (Kosmulski et al. 1999). Colloidal particles like clay particles, in the aqueous medium, usually exhibit higher zeta potential at high pH, at which particles show good dispersibility as the electrostatic repulsion becomes stronger. However, as the zeta potential registers close to zero, the particles become unstable and are a

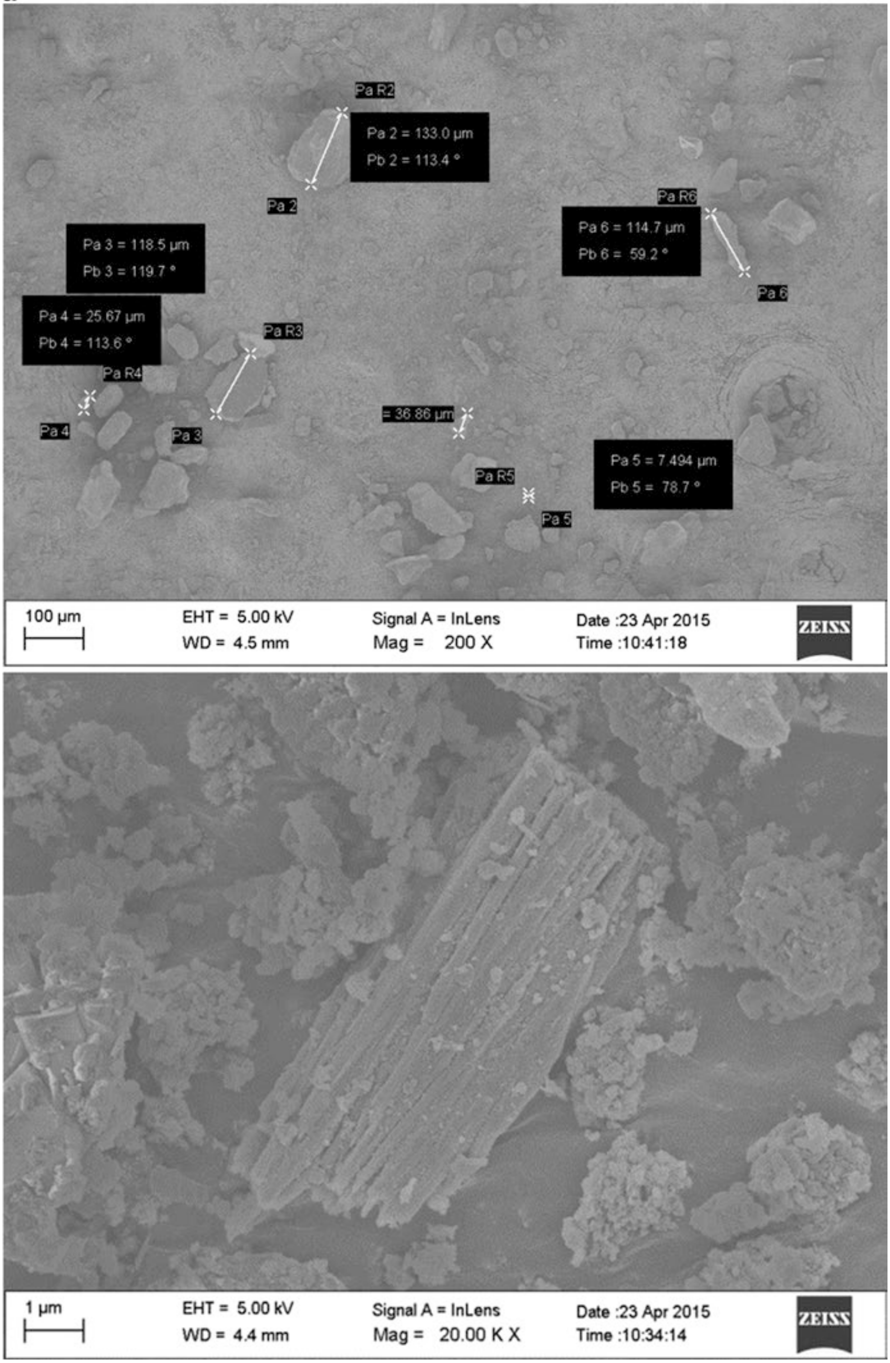


Fig. 8.1a SEM images of red mud waste depicting irregular shaped particles

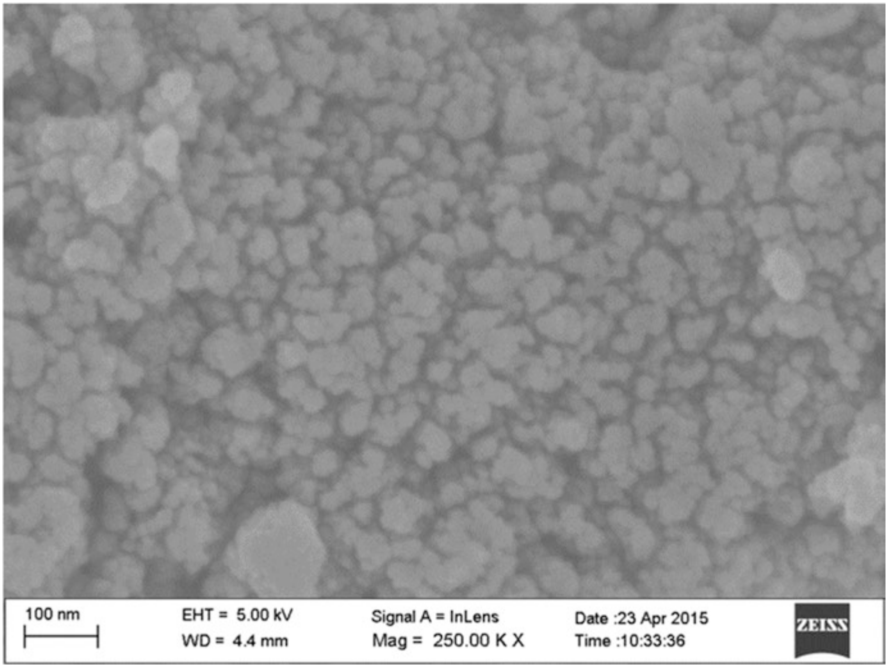
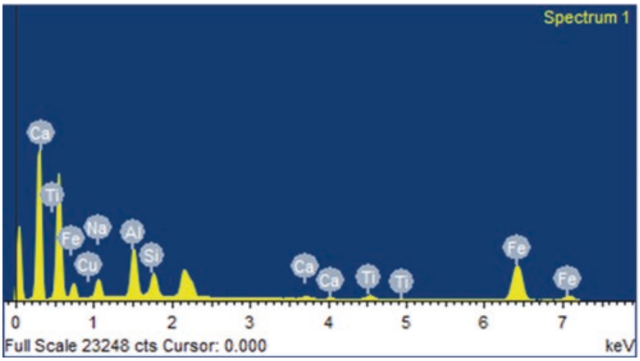


Fig. 8.1a (continued)



Element	Weight (%)
Na	13.53
Al	20.82
Si	10.65
Ca	1.32
Ti	2.80
Fe	49.36
Cu	1.53
Total	100.00

Fig. 8.1b Elemental analysis by EDS showing major elements of red mud waste

likely to aggregate as the pH of the aqueous medium decreases (i.e. more acidic). The relationship between suspension stability and zeta potential values is provided in Table 8.2.

Ionic bond, van der Waals forces and covalent bond kind of behaviour in the presence of water are critically dependent on the surface charge of the constituent particles. Similarly, other properties like rheology, ion exchange capacity, pH buffering capacity and adsorption capacity are also highly dependent upon the

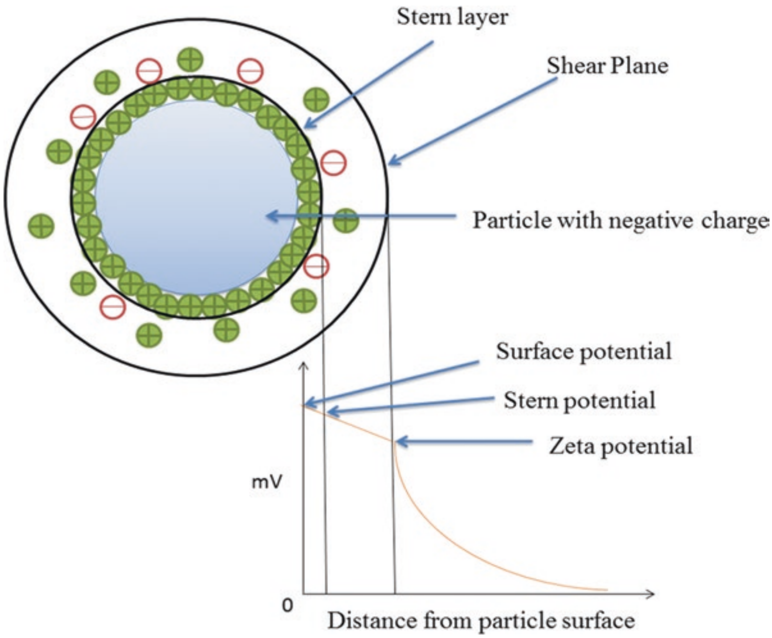


Fig. 8.2a Schematic view of zeta potential of a particle in suspension

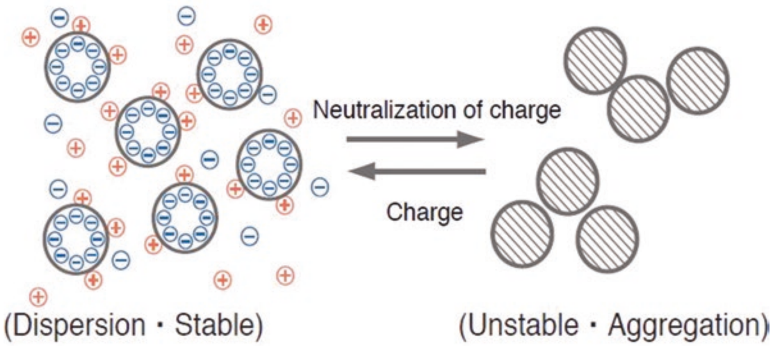


Fig. 8.2b Flocculation or dispersion mechanism of suspended particles

surface charge properties of individual particles (Gräfe et al. 2011). The complete understanding or characterization of any material, establishment of its surface charge properties, is very important (point of zero charge or isoelectric point).

Generally, these properties either in individual or in their combination largely control the mechanical behaviour or performance of neutralization or stabilization processes of the red mud waste. Thus, measurement and understanding about the surface charge properties help in to deal with the waste in field application perspective.

Table 8.2 Relationship between suspension stability and zeta potential value

Zeta potential (mV)	Stability behaviour of colloid
+3 to 0	Maximum agglomeration and precipitation
−1 to −4	Excellent agglomeration and precipitation
−5 to −10	Fair agglomeration and precipitation
−11 to −20	Threshold of agglomeration
−21 to −30	Plateau of slightly dispersion
−31 to −40	Moderate dispersion
−41 to −60	Good to very good dispersion
−60 to −80	Excellent to maximum dispersion

Riddick (1968)

In addition, the understanding of surface charge characteristics may obviously facilitate in identifying an appropriate additive, which would be effective in neutralizing and/or stabilizing the waste.

8.1.3 Theory on Measurement of Zeta Potential

8.1.3.1 Henry's Equation for Measuring Electrophoresis

When an electric field is applied across an electrolyte, charged particles suspended in the electrolyte are attracted towards the electrode of an opposite charge. However, viscous forces acting upon the particles tend to oppose this movement. When an equilibrium is reached between these two opposing forces, the particles move with a constant velocity. The velocity with which a particle under constant electric potential moves with a certain velocity is referred to as electrophoretic mobility. Knowing the electrophoretic mobility, zeta potential on the particle can be determined using Henry's equation, as expressed below:

$$U_{\mathrm{E}} = \frac{2\zeta\, f(Ka)}{3\eta} \tag{8.1}$$

where ζ is the zeta potential (mV), η is the viscosity of solution, ε is the dielectric constant, U_{E} is the electrophoretic mobility and f (Ka) is the Henry function.

Similarly, Smoluchowski's formula is a well-known one widely used to determine the zeta potential of particles. The mathematical form of the equation is shown in Eq. (8.2):

$$\zeta = \frac{4\pi\eta}{\varepsilon} \times U \times 300 \times 300 \times 1000 \tag{8.2}$$

where ζ is the zeta potential (mV), η is the viscosity of solution, ε is the dielectric constant and U is the electrophoretic mobility.

8.1.4 Objectives

The objective of this study is to understand the behaviour of the red mud waste of Indian origin from zeta potential measurements and interpret the surface charge behaviour such as flocculation or dispersion from these measurements. In addition, average particle diameter under varying pH conditions was measured to confirm the formation of flocculation or dispersion phenomenon in the particles. The study gains significant practical importance, particularly in the viewpoint of neutralization or stabilization of red mud waste using commercial chemicals or industrial solid wastes/by-products.

8.1.5 Zeta Potential Measurements

Zeta potential measurements were performed using Zetasizer Nano ZS90 (made in Malvern, UK). The device uses laser Doppler electrophoresis technique to measure the zeta potential, ζ, of a sample. While carrying out the measurements, an electric field is applied to suspension molecules, causing the particles move with a velocity related to their zeta potential. This velocity is commonly referred to as electrophoretic mobility, which is measured by a laser interferometric technique using laser Doppler velocimetry (LDV). With the knowledge of known electrophoretic mobility and the applied electric field, along with two more constants of the sample, that is, viscosity and dielectric constant, zeta potential of a sample is calculated using Henry's equation. Each measurement is the mean of 20 runs, each of which was averaged over three individual measurements performed automatically by the instrument. Measurements were conducted on suspensions of the red mud waste prepared with liquid to solid (L/S) ratio of 50 and 100, respectively, at time intervals of 0, 30, 60, 120 and 240 min by setting the refractive index and adsorption of the instrument as 2.55 and 1, respectively. All the measurements were performed on suspensions maintaining pH values ranging from 1 to 10. Volume of HCl/NaOH solutions required to attain the desired pH values of red mud suspension is prepared by mixing the corresponding aqueous solution with distilled water as per the calculated proportions. The suspensions were taken in a disposable polystyrene cuvette cell, which would then carefully be inserted into the cuvette holder during the measurement. Figs. 8.3a and 8.3b depicts the schematic view of the measurement of zeta potential of a sample.

The Zetasizer is also equipped with capability of measuring grain sizes within the range from 0.3 to 5000 nm. A typical dynamic light scattering (DLS) at a

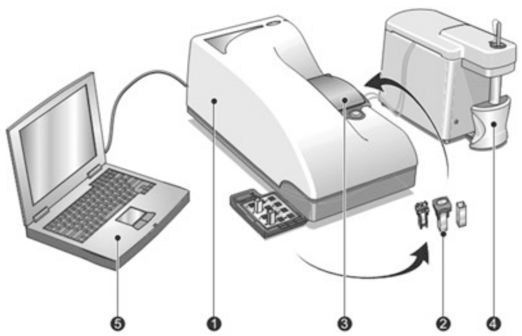


Fig. 8.3a Zeta potential instrument *1* Zetasizer Nano optical unit, *2* cells, *3* cell area, *4* MPT-2 titrator, *5* computer running the Zetasizer software

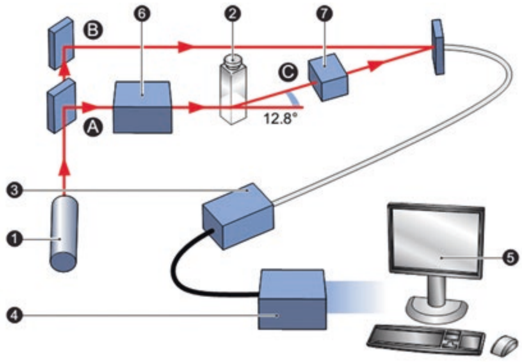


Fig. 8.3b Enumeration of steps in measurement of zeta potential of sample (Malvern 2009) *1* laser, *2* cell, *3* detector, *4* digital signal processor, *5* computer, *6* attenuator, *7* compensation optics

scattering angle of 90 is used to measure the particle diameter. This technique measures the diffusion of particles moving under Brownian motion in suspension, which would subsequently be converted into mean diameter using the Stokes-Einstein relationship. Each data value is the mean of 15 runs, each of which is an average of three measurements. Average particle diameter was measured for each L/S ratio corresponding to pH ranging from 1 to 10.

8.2 Materials

The red mud waste used in the present study belongs to NALCO's alumina refinery plant located in Damanjodi, Koraput, Odisha, India. The physical, chemical and mineralogical properties were established on the samples in accordance with the guidelines outlined in respective standards.

8.3 Results and Discussion

8.3.1 Properties of Red Mud

The summary of physical, chemical, mineralogical and geotechnical properties of the red mud waste is presented in Table 8.3. The physical and geotechnical properties are widely used in the identification and classification for any soil type in the field of geotechnical engineering. The specific gravity, G_s, one of the most important properties of the red mud, is measured as 3.05. The value is obviously considerably higher than the natural soils. The red mud waste mainly comprises of oxides/minerals of iron family (i.e. goethite and hematite) in a significant amount, leading to show high value of specific gravity. Figure 8.4 shows the gradational characteristics of the red mud waste. It can be seen from the graph that 95% constituent particles of the waste are falling under the fine-grained category (i.e. <75 μm), with a clay size fraction of 27% and silt size fraction of 68%. The majority of particles in the red mud waste are silt size range. Since the waste constitutes with silt to clay range particles, Atterberg's limits were established for this waste, as listed in Table 8.3. The liquid and plastic limits were determined as 41% and 36%, respectively, and plasticity index was calculated as 5%. Although the waste comprises of a reasonable amount of clay size particles, plasticity behaviour is confined to a very narrow range of water content. From the consistency limits and gradational characteristic properties, the red mud is classified as silt of low plasticity, ML, soil. The other properties show that the red mud waste has high pH ranging from 10.7 to 11.5, high specific surface area ranging from 41.6 to 47.2 m^2/g, low pore volume and high pore radius. Mineralogical analysis shows that Fe and Al group minerals are dominated in the red mud waste.

The various minerals identified in the red mud waste are listed in Table 8.3. It is worth noting that the waste does not compose of minerals, which are typically found in conventional soils like clays and sandy soils. Even in the absence of clay-like minerals, red mud waste still exhibited plasticity characteristics.

Table 8.3 Physical, chemical, geotechnical and mineralogical properties of RMW used in the study

S. no.	Property	Value
1.	Specific gravity	3.05
2.	Consistency limits (%)	
	Liquid limit	41
	Plastic limit	36
	Plasticity index	5
3.	% fractions	
	Sand	5
	Silt	68
	Clay	27
4.	pH	10.7–11.5
5.	USCS	ML type
6.	SSA (m^2/g)	41.57–47.20
7.	Pore volume (cc/g)	0.083–0.097
8.	Pore radius (Å)	17.47–20.99
9.	Chemical compositions	
	Fe_2O_3	48.90
	Al_2O_3	18.96
	SiO_2	18.35
	Na_2O	4.80
	TiO_2	3.69
	CaO	1.52
	K_2O	1.05
	P_2O_5	0.64
	SO_3	0.54
	MgO	0.50
	Cl	0.45
	Others	0.60
10.	Mineralogical compositions	Calcite, goethite, gibbsite, hematite, ilmenite, magnetite, perovskite, rutile, sodalite

8.3.2 *Zeta Potential of RMW*

Initial attempts are made to establish the stability time at which the value of ζ becomes constant for a given liquid to solid, L/S, ratio. Two L/S ratios (i.e. 50 and 100) are considered for the testing purpose. Figure 8.5 depicts measured zeta potential values with time at L/S ratios of 50 and 100, respectively, under variable pH conditions.

Trends in Fig. 8.5 show that ζ values become stabilized after approximately 120 min, corresponding to L/S ratio of 100, only, whereas the values found remain fluctuating corresponding to L/S ratio of 50. Thus, all zeta potential measurements are

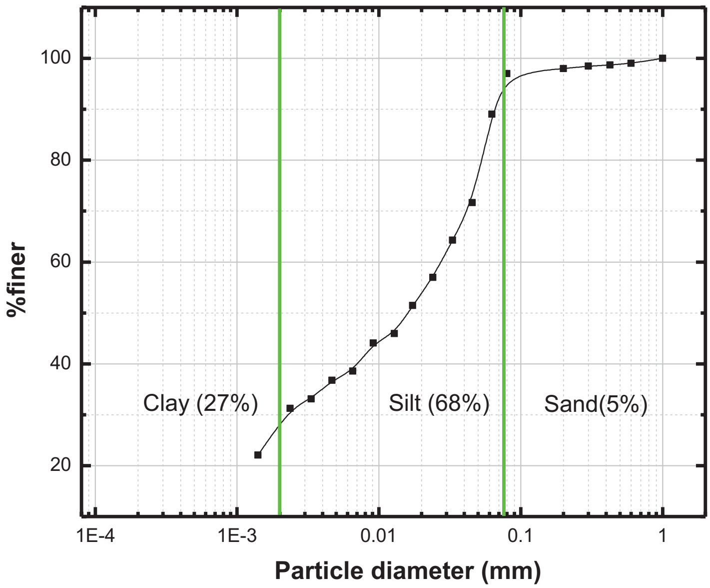


Fig. 8.4 Gradational characteristics of red mud waste used for the study

carried out considering L/S ratio of the suspension as 100. Further, results show that the value of ζ did not remain constant with change in pH. In fact, studies document that pH is an important and critical parameter that affects the zeta potential and, hence, the surface charge properties of a material. For a much better understanding, the variation of ζ with pH is plotted, as depicted in Fig. 8.6.

From the figure, it can be observed that ζ increased with pH up to a certain pH value of 4 and then decreased steadily beyond this pH value. It is obvious from the results that ζ becomes more negative when the pH of suspension exceeds 6.6 and becomes more positive when the pH of the suspension is below this value. Generally, the adsorption of H^+ and OH^- ions onto the surface of the particles is responsible to changes in the surface charge characteristics of a material (e.g. zeta potential value). The more positive or more negative values of ζ with variation in pH may be attributed to dominant adsorption of either H^+ or OH^- ions on the particle surface, depending upon the pH of the suspension.

In acidic condition, H^+ ion concentration is prominent, and hence, adsorption of these ions on the particle surfaces dominates, leading to positive values of zeta potential. Contrarily, in basic condition, the amount of OH^- ion availability becomes predominant, and therefore, the zeta potential decreases, leading to negative value. Ideally, this could have been occurring in the suspension with change in pH, leading to the red mud waste showing both positive and negative values of the zeta potential, as presented in Fig. 8.6.

From Fig. 8.6, it can also be seen that at pH equal to 6.6, ζ becomes zero. The point at which ζ becomes zero is called as point of zero charge, PZC, or isoelectric

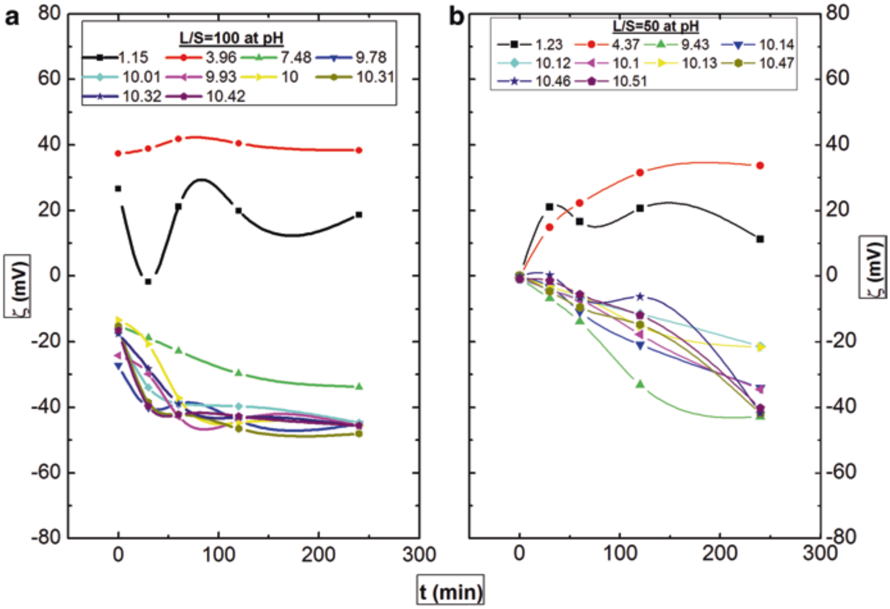


Fig. 8.5 Establishment of stability time for measurement of zeta potential (**a**) L/S = 100 and (**b**) L/S = 50

point, IEP. Generally, the PZC is the point where the colloidal system is least stable. At PZC/IEP, molecules carry no net charge on their surfaces. In other words, at this point the total positive charge becomes equal to the total negative charge. The significance of the PZC/IEP is that it can affect the solubility of a molecule at a given pH. Moreover, the tendency of particles to agglomerations becomes pronounced at PZC. A maximum ζ value of +41.8 mV and −48 mV is recorded at pH of approximately 4 and above 10, respectively, for red mud waste. This maximum positive and negative value of zeta potential is a clear indication for the red mud waste possessing the surface charge characteristics. A range of zeta potential values with a likely inference, which can help in identifying the behaviour of charged particles such as formation of flocculation or dispersion, is also depicted in the graph. It can be inferred from the constant ζ value of −48 mV that the particles of the red mud waste show 'good to very good dispersion' when the pH is above 8. This finding has a tremendous practical significance, as it advocates that pH of red mud during its neutralization or stabilization with a suitable additive needs to be maintained at least above 8, in order to obtain the benefit of particles interacting liberally with the added additive(s).

As such, studies report that the surface charge properties are strongly dependent upon the mineralogical composition of a material. For example, in the case of layer-silicate minerals (such as clays) due to the substitution of Al^{3+} for Si^{4+} in the silica tetrahedral and Mg^{2+} for Al^{3+} in the octahedral layer of the crystal lattice, resulting

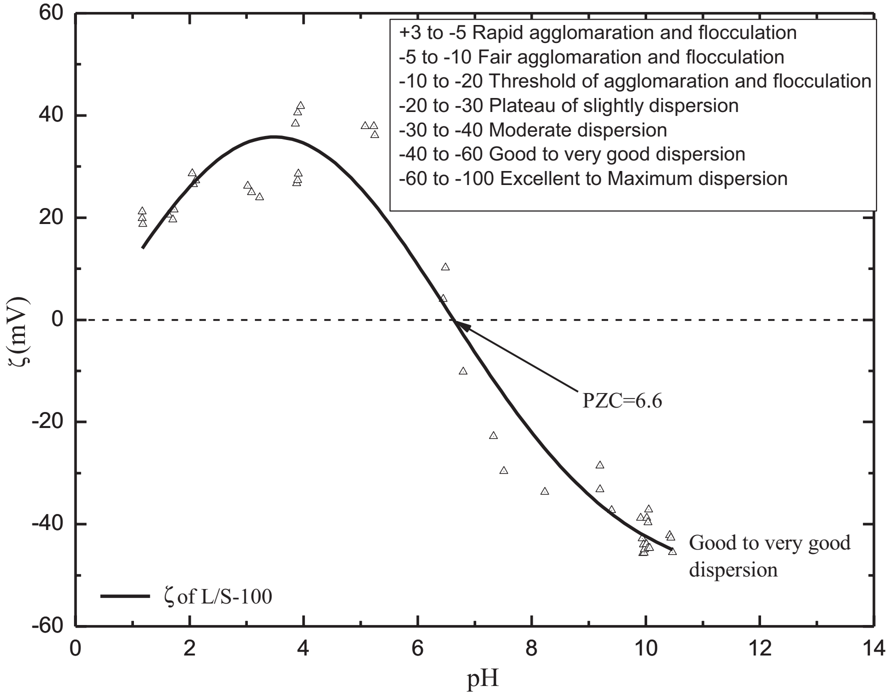


Fig. 8.6 Variation of zeta potential with pH

in surfaces of these crystal faces carries a constant negative charge that is independent of solution conditions (Fuerstenau and Pradip 2005). The typical oxide compositions of the red mud consist of iron, aluminium, silica, titanium and calcium (refer to Table 8.3), and they are available in mineral forms like hematite, calcite, goethite, gibbsite, sodalite, ilmenite, magnetite, perovskite and rutile. The constituent chemical and mineralogical compositions (Fe-, Al-, Ti- and Si-related oxides and minerals) of red mud clearly suggest the existence of pH-dependent variable charge and permanent charges on the surfaces of particles. As such, isomorphous substitution for Si, Al and Fe in desilication products (such as sodalite) can result in permanent charge on the surfaces of particles of red mud.

In order to further validate the finding of PZC at pH of 6.6 (refer to Fig. 8.6) for RMW, the relevant data have been searched for in the literature corresponding to different mineral types as well as for the red mud produced by different sources. The data compiled are listed in Tables 8.4 and 8.5, respectively. The values in Table 8.4 evidently highlight that minerals, particularly constituted with Fe and Al, exhibited PZC in the pH range from 6 to 8. This observation well corroborates vis-à-vis with the results reported in Fig. 8.6. As such, results depicted in Fig. 8.6 demonstrate that the red mud maintains the neutral character, which is nearly analogous to Fe and Al mineral groups (e.g. goethite, hematite, gibbsite, rutile, magnetite). Further, values

Table 8.4 The values of pH at which PZC/IEP reported for various mineral and oxide compositions present in red mud waste

Mineral/chemical oxide	pH range	References
SiO_2	1.9–2.5	Kosmulski (2002) and Liu et al. (1993)
TiO_2	5.1–6.4	Kosmulski (2009a)
Al_2O_3	7.9–9	Liu et al. (2013) and Kosmulski (2002)
Fe_2O_3	8.03	Liu et al. (2013)
Quartz	2.3–2.8	Kosmulski (2009b)
Hematite	6.0–9.2	Kosmulski (2002, 2009a)
Magnetite	5.7–6.8	Kosmulski (2002, 2009a)
Goethite	6.6–8.6	Kosmulski (2002, 2009a)
Calcite	8.2	Somasundaran and Agar (1967)
Gibbsite	6.5–8.3	Kosmulski (2002, 2009a)
Rutile	5.3–5.6	Kosmulski (2002, 2009a)
Perovskite	8.1	Hanawa et al. (1998)

Table 8.5 Values of pH at which PZC/IEP reported for red mud produced by different sources

Red mud/bauxite source	pH range	References
Weipa, Claremont	6–7.8	Chevdov et al. (2001)
CHALCO, China	7.5–8.2	Kun-yu et al. (2008)
Chinese RM (CHALCO)	7.1–8.7	Liu et al. (2013)
Rio Tinto Alcan, Yarwun refinery, Australia	6.3–6.8	Liu et al. (2013)
San Ciprian, Spain	6.9	Lopez (1998)
Overall	6–8.7	–

in Table 8.5 show an excellent agreement between the results of present study and those of red mud produced by different sources, with regard to the value of pH at which PZC/IEP occurs.

8.3.3 Particle Size Characteristics

Usually, the stability of suspensions can be assessed from the zeta potential, which in turn varies with the particle size. On the other hand, surface charge properties are also dependent upon particle size and pH of the suspension. Thus, any change in surface charge characteristics can in turn lead to change in the zeta potential, which in turn dominates the stability of particles in the suspension by forming agglomerations or dispersions. One of the means of confirming the particle affinity to agglomeration or dispersion is the measurement of their diameter. As such, the average particle diameter measured at different pH levels and is drawn against measured zeta potential is depicted in Figs. 8.7 and 8.8, respectively. The intensity/distribution of particle sizes captured as a function of pH and L/S ratios is shown in Fig. 8.9.

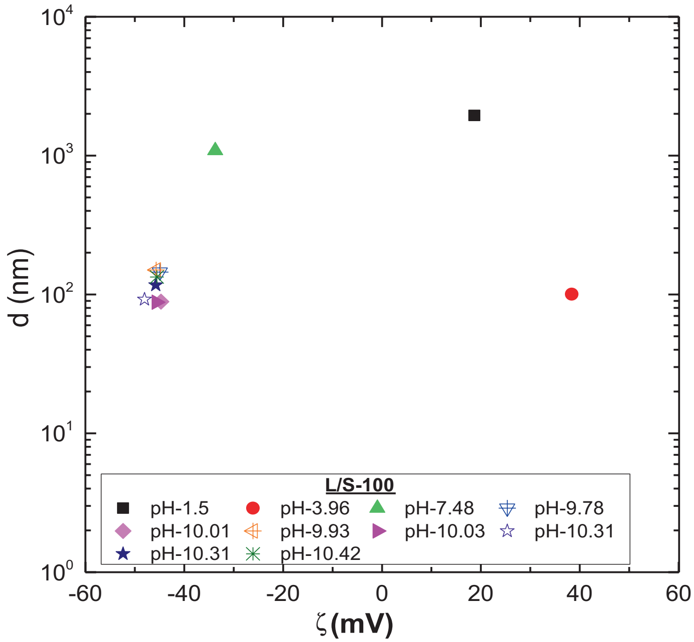
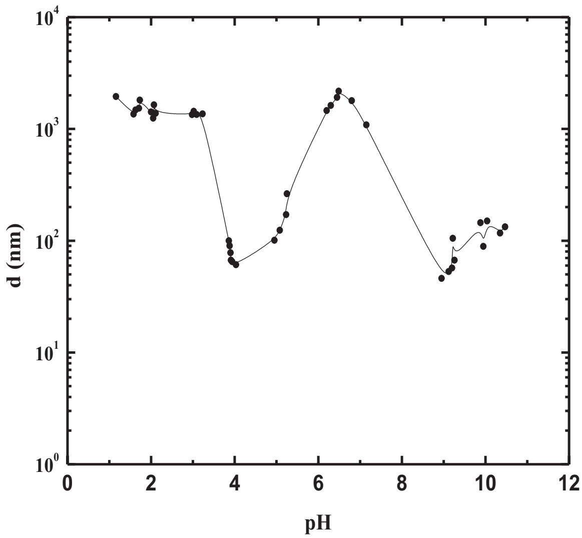


Fig. 8.7 Observed average particle diameter with zeta potential at different pH conditions

Fig. 8.8 Variation of average particle diameter at different pH conditions



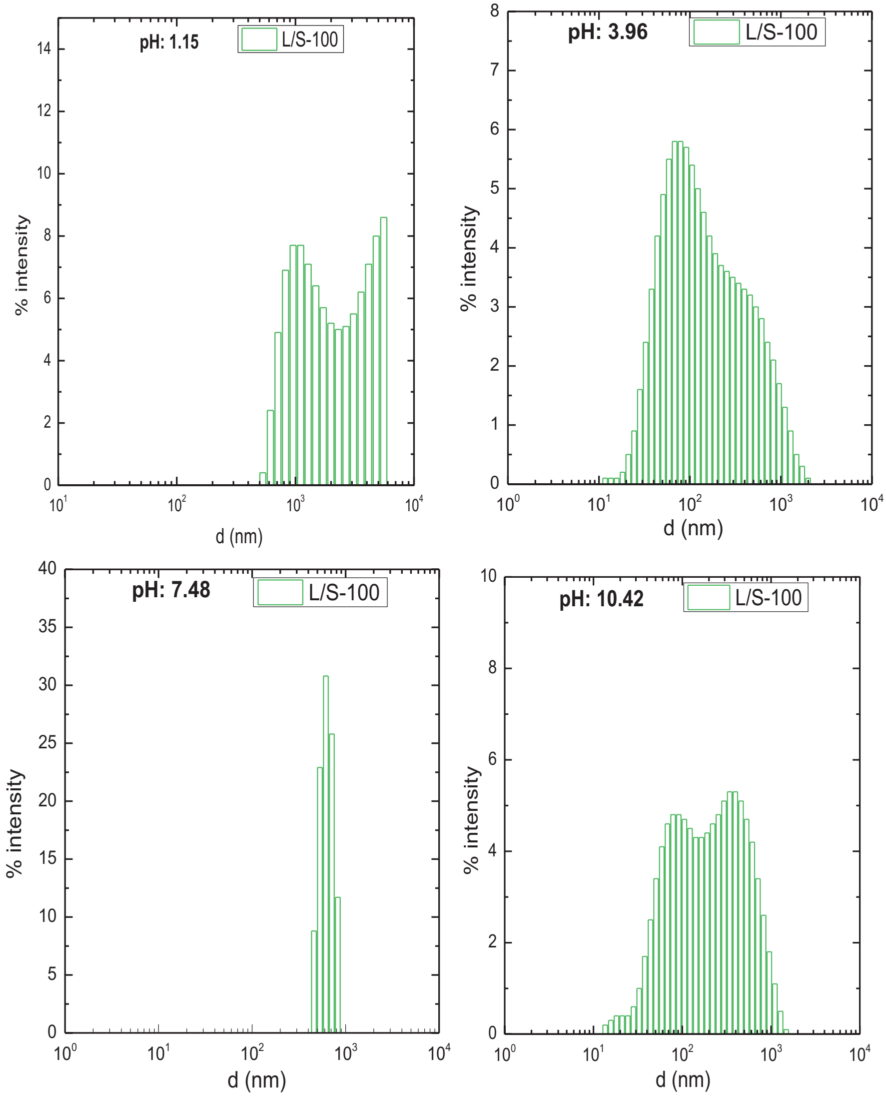


Fig. 8.9 Variation of particle intensity at different pH levels

It is apparent from Figs. 8.7 and 8.8 that at extremely low pH value (i.e. 1.15), PZC and neutral pH value (i.e. at 7.48), an average particle diameter of approximately 1660, 2176, and 1080 nm was recorded. However, for the remaining pH values, average particle diameters of 65–150 nm were observed. The lesser average particle diameter is a clear indication of the dispersive characteristics by the particles. This finding validates the inference made in Fig. 8.6 that the red mud waste particles exhibit 'good to very good dispersion' characteristics. On the other hand, the greater average particle diameter clearly delegates the tendency of the particles to agglomerate, which could be due to coulombic attraction or van der Waals forces on the particles.

8.4 Applications and Practical Significance of Zeta Potential Measurements

- Zeta potential measurements are directly related to the character and structure of the electric double layer at the particle-liquid interface.
- Clays and clay-type materials, usually, have negatively charged faces and positively charged edges. The physical properties such as sedimentation, viscosity and structural strength are enormously responsive to the electric double layer around the particles and the affinity of the particles to aggregate. Zeta potential measurements give particularly relevant information where colloid stability and/or ion adsorption is involved.
- Zeta potential behaviour of suspension can be related to geotechnical properties such as compaction, swelling characteristics, shear strength, consolidation and material of clay-like behaviour of waste materials.
- Control of the mechanical behaviour of suspensions, using additives in the liquid phase, is also an important feature of solid and industrial waste treatment and waste neutralization and other processes of clay-like materials.

8.5 Summary

The study presents systematic investigations related to the surface charge and particle size characteristics of red mud waste from the zeta potential measurements under variable pH conditions. The following general conclusions can be drawn from the results of the study:

- The values of zeta potential found varying over a wider range from +41.8 mV to −48 mV, clearly demonstrating that the red mud waste possesses surface charge characteristics. Apparently, measurements also showed strong dependence on pH of the suspension.
- The results highlight that ζ increases with pH up to a certain pH value of 4, and thereafter, it decreased continuously with the further increase in pH.
- The PZC/IEP, which indicates the neutral character of red mud waste, was found at pH of approximately 6.6.
- The results highlight that the waste exhibits ‘good to very good dispersion’ characteristics when the pH of the suspension is maintained at 8 or above.
- An average particle diameter of 65 nm, at pH of 3.96 and above 9.00, and 1660 nm and 1080 nm, at pH of 1.5 and 7.48, was recorded.

The results reported in the study bears very practical significance pertaining to neutralization or stabilization is concerned, in selection of a suitable additive for stabilization, and in comprehending the rheological behaviour of red mud waste.

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