

A rapid technique for measuring oxidation-reduction potential for solid materials

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ABSTRACT

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Oxidation-reduction potential, Portable ORP meter, Normalized hydrogen electrode and Pumice tuff

Access by Smart Phone



The present study proposes a rapid measurement technique of oxidation-reduction potential (ORP) of solid materials. With the conventional portable ORP meters, the proposed procedure includes a) grinding of solid and sieving to a homogeneous grain size, b) making slurry with di-ionized water at a definite solid-solution ratio, c) shaking and centrifuging of the slurry at some intervals until maximum ORP values obtained. The changes of ORP values by this rapid method were found clearly distinguishing between oxidized and fresh rock type.

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I. Introduction

The ORP, indicated by 'Eh' and expressed in millivolt (mV), is the measure of the tendency of a chemical species to acquire electrons and be reduced. It is a "potential" electrical energy in liquid that is stored and ready to be put to work. This potential is used to determine oxidizing or reducing conditions in water or soil, and to predict the states of different dissolved metals in water. In environmental situations, it is

common to have complex non-equilibrium conditions between a large number of chemical species, which is difficult to make accurate and precise measurements of the reduction potential. However, approximate values can be obtained from the measurements and the conditions of oxidizing or reducing regime can be defined (VanLoon 2011). Generally, the oxidizing condition of solution possesses the positive ORP values and reducing conditions shows the negative values. The more positive the potential, the greater the species' affinity for electrons.

While the redox potential value is a common measurement in water quality, the Eh-pH diagram is widely used for solid analysis as well. Specially, for the assessment of stability fields of minerals and dissolved species, the redox potential values are indicative to the environmental condition the solid is included. In an Eh-pH diagram, the solid stability area is related to the saturation condition, and dominant aqueous species gives fundamental information on sorption and colloid phenomena as well as surface characteristics of materials (Takeno 2005). Eh-pH diagrams are thus essential to understanding solute and radionuclide transport in groundwater. This ORP value also tells the potential weathering condition of the geological formation in the subsurface (Yoshida et al. 2008).

Eh measurement of soils in field condition using portable ORP meters is widely used by penetrating the electrodes in the loose soil (Fiedler et al. 2007). The application of microelectrode techniques for this purpose also has been adopted for better measurement of soil ORP (Zhang and Pang, 1999). In-situ ORP measurement in a thick glacial overburden is also reported, however, that includes the measurement in sand slurry (Hamilton et al. 2004). In laboratory experiments with loose soils under various artificial environmental conditions, ORP values can be determined using portable or benchtop ORP meters (Parveen et al. 2017).

Although, effect of pH and redox potential are very significant for the study of the solubility of heavy metals (Chuan et al. 1996) that not only can contaminate the soils, but also to any kind of hard bed rocks that contain ground water. This kind of study is particularly important for country like Bangladesh which has extremely high arsenic contamination problem as arsenic speciation and solubility also depends on redox potential and pH (Masscheleyn et al. 1991). However, the reported techniques can only be applied for loose soils and not for any type of rocks which are not loose enough and electrode cannot penetrate. No reports were found to measure the redox potential for hard type solid and especially for the samples which were collected long time ago and needs to measure in the laboratory. The question remains whether after the time gap from sample collection to measurement, the ORP value still reflects the field condition. Therefore, measurement technique should have the ability to represent actual redox potential value that could match the in-situ environmental condition.

II. Materials and Methods

A rapid technique was adopted for the ORP measurement using portable ORP meter in laboratory in the present study for solid. Fresh and oxidized pumice tuff from northern part of Honshu Island of Japan was used as model solid. The samples were collected during the excavation at the subsurface during the year of 2010. The location of sampling point was at the boundary line of two zones where oxidation phenomena was evident due to water-rock interaction. The solid phase was analyzed and found to be similar in mineralogical and chemical composition with variation in physical properties like porosity and pore size distribution (Rajib et al. 2015, 2016). The oxidized part differs in color from the fresh tuff, although some fresh like parts were found to be affected by oxidation. For this experiment, 4 g of fresh and oxidized pumice tuff powder of less than 150 μm was mixed with 40 ml di-ionized water (DI) having the solid-solution ratio is 1:10. Slurry was hand-shaked for about 3 min to mix all the grains with water properly and kept for 10 minutes to settle all the grains. Then ORP was measured. Furthermore, slurry was automatically shaken using a shaker (SRR-2 type, AS One Co.) at around 100 rpm for 15, 30, 60 and 180 min. After each shaking, samples were centrifuged for 5 min at 3000 rpm, to separate the solid from solution and ORP was measured. Observing the changes of ORP values after each shaking, samples were kept for 1, 2 and 5 days and ORP was measured. Besides ORP, pH was measured at all steps and observed that pH did not change significantly. Total experiment was done in triplicate and average was taken to minimize error and also compared with di-ionized water whose ORP was measured simultaneously. A generalized flow chart of the proposed method is shown in Figure 01.

The Eh value was measured using a portable ORP meter (Model WM-22EP, TOA DKK Co.; [Figure 02](#)). The system contains 3.3 mol/l AgCl reference electrode compared with a redox test solution containing quinhydrone powder and phthalate pH solution. Measured Eh values were corrected to normal hydrogen electrode (NHE) using following equation ([Okada et al. 1958](#); [Matsushita et al. 1974](#)).

$$Eh_{NHE} \text{ (mV)} = Eh \text{ (mV)} + 206 - 0.7(t - 25)$$

Where “t” is temperature in degree Celsius.

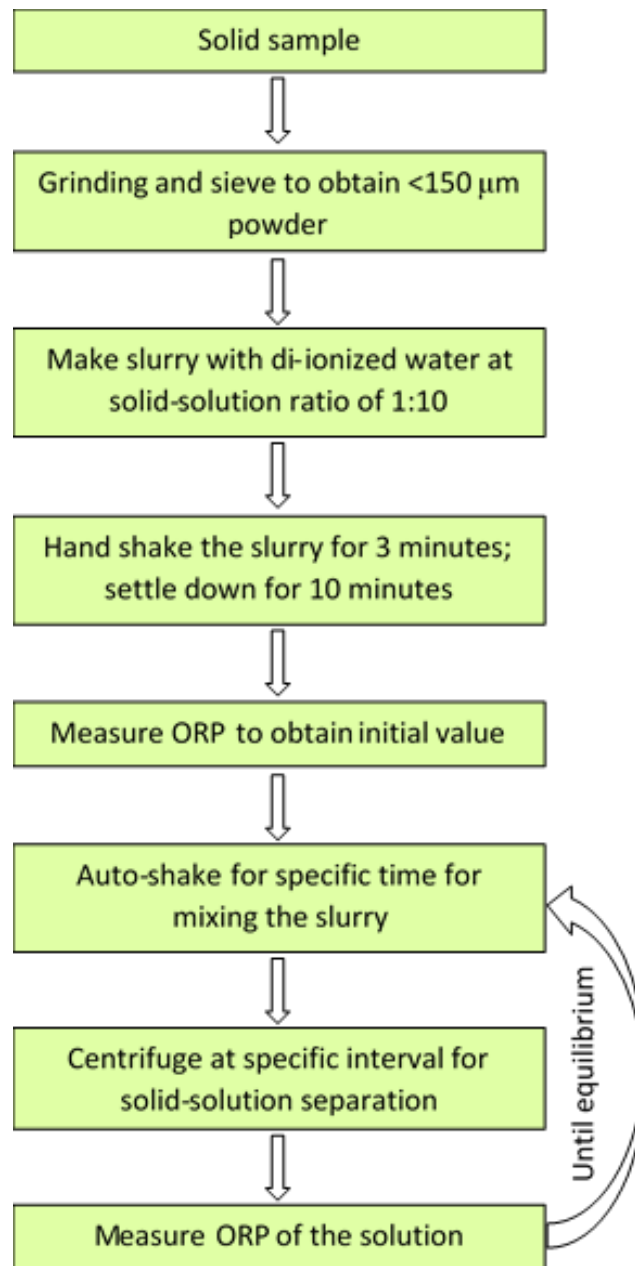


Figure 01. Generalized flow chart of the proposed method.



Figure 02: Measurement with the portable ORP meter.

III. Results and Discussion

Eh_{NHE} was found as positive values indicating in the state of quite strong oxidizing condition of both solutions (Figure 03a). The values were found linearly increased at initial time of the experiment. However, with the saturation of dissolved metal, the ORP starts to become equilibrium. With decreasing pH, Eh was found to be increased for different solid, however, Eh did not depend on pH for same solid. Fresh tuff, with pH of around 8-9 have the considerably lower ORP values (429-513 mV) than oxidized tuff (540-649 mV) with pH of around 4.5 (Figure 03b). The similar results are also stated in the report of Rokkasho tuff by Oyama et al. (2007). While comparing with di-ionized water Eh_{NHE} values (476-526 mV) used in the same experiment, the values clearly differentiate the variations of ORP of oxidized and fresh tuff condition.

The results of the proposed method present somewhat a semi-quantitative ORP of the solid. Although the values obtained in the experiment are quantitatively presented, the values may not match the real redox potential of the solid. Instead, it could be stated as relatively oxidized or reduced to other solid and hence, considered as semi-quantitative. However, it should be noted that these values may differ from the measurement in field condition as the samples were collected and stored and hence the surrounding environment could change significantly. It is worth mentioning that the redox potential is a temperature sensitive measurement, however, ORP instruments are not temperature compensated. Consequently, the media temperature should always be recorded at the same time as the ORP is recorded. Likewise, as ORP is often pH dependent, they should be recorded simultaneously. (US-EPA 2013). Using the proposed technique, both pH and EC was measured until equilibrium for a research as presented in Figure 04.

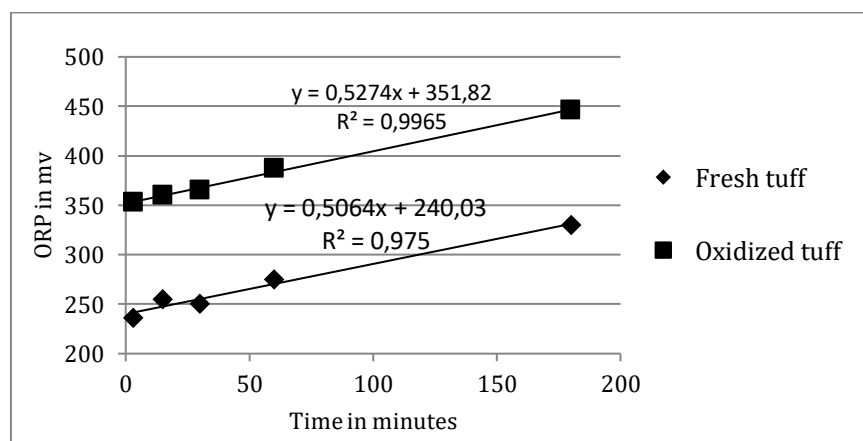


Figure 03a. Linear increase of ORP values at initial hours for both fresh and oxidized tuff.

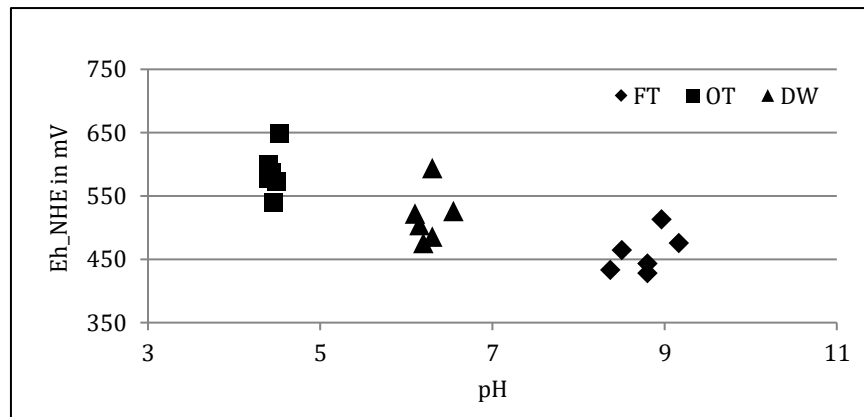


Figure 03b. ORP values of fresh tuff (FT) and oxidized tuff (OT) with respect to pH after correcting to normal hydrogen electrode; also compared with di-ionized water (DI).

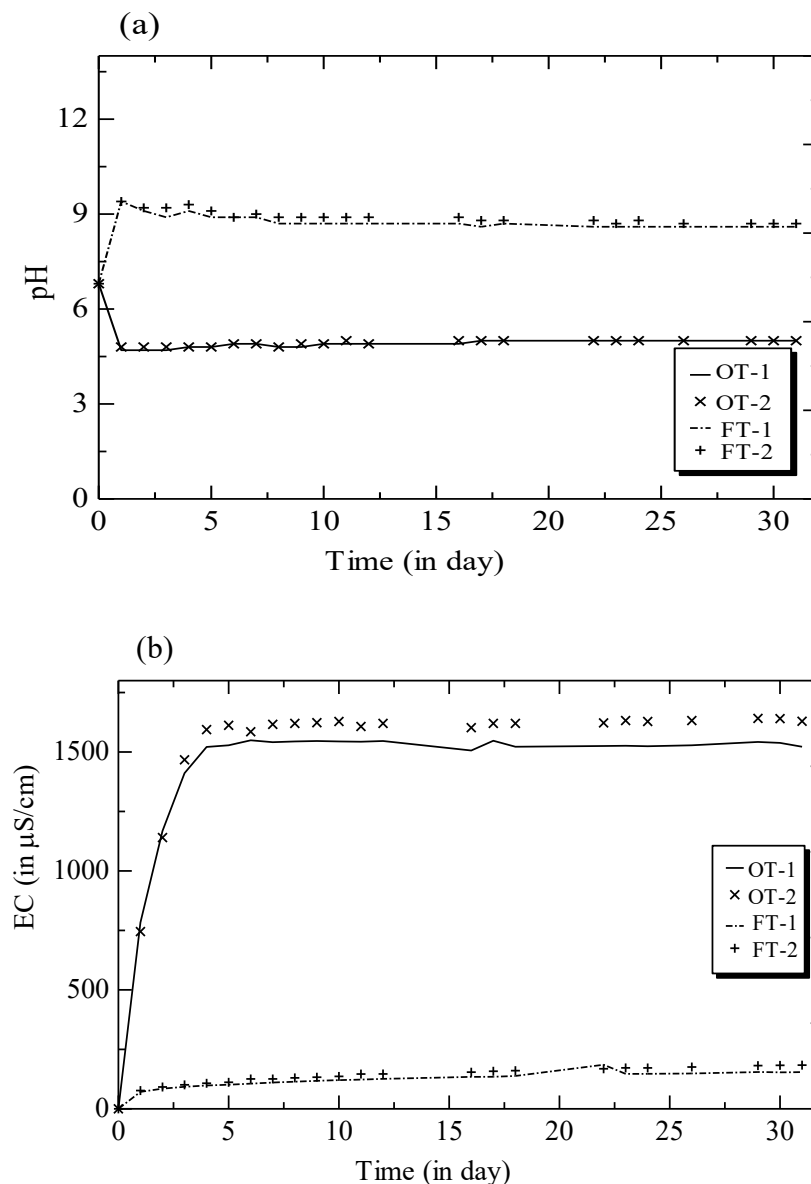


Figure 04. Equilibrium pH (a) and EC (b) of oxidized (OT) and fresh (FT) pumice tuff using the proposed technique (Rajib et al. 2015).

IV. Conclusion

A rapid technique for ORP determination was adopted for solid materials that were collected nearly a decade ago and needs to measure for laboratory purpose. The results showed quite applicable in the context of significant difference in the redox potential among the materials. The limitation of the study lies in the sample numbers and types, and therefore needs to further research to verify for all types of materials. Moreover, effect of grain size of the powder, solid-solution ratio and shaking time are not considered in this rapid measurement. Those parameters could affect significantly for particular types of solid. Therefore, experiment should be conducted to confirm those effects for better assessment of the result. In addition, in-situ measurements of different samples should be incorporated.

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