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Research paper

Physical and chemical characterization and recovery of potash fertilizer from glauconitic clay for agricultural application

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ABSTRACT

Glauconite is a natural occurring iron-rich, heterogeneous, phyllosilicate rock containing around 4–8% of potash (K_2O) locked in the alumino-silicate matrix. An attempt has been made to develop a complete flow-sheet for the recovery of potash from a typical glauconite sample containing 3.93% K_2O, 10.75% Fe_2O_3, 4.41% Al_2O_3 and 70.35% SiO_2. Initially, the detail physico-chemical characterization and beneficiation study was performed to enrich the potash content from 3.93% to 5.52% by removing free silica. The enriched fraction of glauconite was further processed to recover locked potash through chemical treatment. Potassium recovery by direct acid leaching was found to be very poor and also resulted in simultaneous dissolution of iron. Therefore, a combined sulfation roasting–water leaching process was developed to break the matrix and selectively recover potash. Various parameters such as sulphuric acid concentration, roasting and leaching temperature were optimized to achieve >98% potash dissolution. The potassium from the leach solution was recovered as sulfate of potash (SOP) suitable for fertilizer application.

1. Introduction

Fertilizers play a vital role in supplying nutrients such as nitrogen (N), phosphorus (P) and potassium (K) to the soil which leads to increase in crop production. Potassium is the major univalent cation utilized by all living cells and it is found in higher concentrations in plants as well. Large amount of potassium fertilizer is required for healthy plant growth and also to maximize crop production.

Presently, K- fertilizer obtained from sedimentary rocks such as sylvite, syngenite, carnalite, kainite, polyhalite (mixture of soluble salts, mainly KCl) surface and sub-surface brines. The total potassium content in different potash fertilizer is expressed as equivalent weight (wt) % of K_2O. Countries like Canada, Russia and Belarus produced >90% of world potash on which >150 countries are dependent for supply of potash fertilizer (Anderson, 1985; Manning, 2010; Rawashdeh and Maxwell, 2014). Global potassium capacity is forecast to increase from 45.4 million tons K_2O in 2012 to 59.5 million tons in 2017 with the growth rate of about 3% annually (Heffer and Prudhomme, 2013).

The rising demand for potassium fertilizer from developing nations, experiencing a massive growth of population leads to global sustainability concerns. According to the United Nations, the world's population has increased from 2.5 billion in 1950 to 6.9 billion in 2011 and it is expected to exceed 9.1 billion by 2050. This will lead to an increased need for food grain production. The United Nations Food and Agriculture Organization (FAO) projects that >85% of this additional demand will come from densely populated developing countries. Already K-deficits have been reported for African continent, China and India (Römheld and Kirkby, 2010; Sheldrick and Lingard, 2004). Even many European countries are also facing significant reduction in K use as fertilizer (Öborn et al., 2005; Somerwill et al., 2012). In order to ensure self-sufficiency and reduction in import of potash, exploitation of alternative resources (potassium containing silicate minerals) such as K-feldspar (Bolger, 1995; Ciceri and Allanore, 2015; Hao et al., 2012; Rao et al., 1998), Nepheline syenite (Hussain and Ahmed, 2011; Jena et al., 2014, 2016) and Glauconitic sandstone were considered promising resource to produce potassium fertilizer in the near future.

India with its vast agricultural base supports 17% of global population. Unfortunately, India doesn't have any commercially exploitable resources for potash and currently imports about 5.1 million tons per annum for direct application as well as for production of complex fertilizers. India has huge deposits of K- feldspar, Nepheline syenite and Glauconitic sandstone containing insoluble potassium. Glauconitic sandstone is found naturally available in granular form and therefore it has certain advantage over other minerals (feldspar and nepheline syenite) which are usually blasted out of igneous rock and carefully separated for further treatment. India has vast reserves of >3000 million tones of glauconitic sandstone containing 4 to 8% K_2O (Kumar and Bakliwal, 2005).

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In early days glauconite is mainly used as soil conditioner and for water treatment application. Presently, this mineral has been found a number of other applications such as geological dating, and removal of heavy metals from aqueous solution (Derkowski et al., 2009; Franus and Bandura, 2014). However, till date not much effort has been made for recovery of potash from glauconite for fertilizer application. Therefore, in the present work an attempt has been made to recover potash from an Indian glauconitic sandstone deposit to save valuable foreign exchange and partial substitution of import.

Glauconite is a dioctahedral, potassium, iron-rich, heterogeneous, phyllosilicate mineral $(K,Na)(Fe^{3+},Al,Mg,Fe^{2+})_2(Si,Al)_4O_{10}(OH)_2$. The early stage reviews related to general characterization and mineral properties are made by various researchers (Bentor and Kastner, 1965; Cloos et al., 1961; Galliher, 1935; Grim et al., 1951; Hendricks and Ross, 1941). Work related to chemical, structural and textural properties modification during acid treatment was recently been studied (Fernandez-Bastero et al., 2003; Hassan and Baioumy, 2006; Mervat and El-Shall, 2004; Srasra and Trabelsi-Ayedi, 2000). The detail mineralogical composition of raw as well as thermally treated Indian glauconitic sandstone in different size fraction was studied (Rawlley, 1994).

In search of an alternative to marine evaporative deposits of potash, lots of attempt has been made since early nineteenth century by most of the countries. For one reason or another, due to use of costly treatment steps such as alkali fusion, chloride and fluoride aided leaching and high temperature valorization, to recover low value market products of potash was probably not possible (Choudhuri et al., 1973; Rao et al., 1993; Sharma et al., 1979; Yadav and Sharma, 1992; Yadav et al., 2000). After careful study of these attempts and availability of highly soluble potash (up to 63% K_2O) in the world, the problem of the extraction of potassium from glauconitic sandstone is fair way to solve by giving attention to recovery of valuable by-products also.

Therefore, sulfation roasting –leaching process was developed to selectively leach potassium along with recovery of iron oxide as by-product. Several researchers have also reported this method for processing variety of other raw materials such as lateritic ore, iron-boron magnets, bauxite residue and spent catalysts for metal recovery (Borra et al., 2016; Guo et al., 2009; Önal et al., 2015; Park et al., 2012; Swamy et al., 2003). In the present investigation, the effect of different process parameters including the amount of sulfuric acid added, the roasting temperature, dissolution temperature and time were studied. The paper mainly aims to achieve quantitative potash recovery with minimum dissolution of matrix phase such as silica, iron and alumina. The residue was further treated to enrich bright red color iron oxide for application as coloring agent in cement industries.

2. Materials & method

The Glauconitic sandstone samples used in this study were collected from the Guneri area of Kuchchh district, Gujarat (India). The location index of this area is of latitude (23°47′02″) and longitude (68°50′47″). The Sample collected from the trench (Fig. 1a) was found to be composed of green, pale and yellowish green supported grains (Fig. 2b).

The collected sample was first crushed to below 2360 μm by using simple laboratory muller grinder. The size analysis of as received sample was performed by using standard screens. A representative sample from the total bulk was selected by conning and quartering method and passed through a Standard Sieves of -150 μm for detail characterization studies. Chemical analysis of all the major and minor elements present in the sample was analyzed by using Bruker X-ray fluorescence spectroscopy (XRF) operated at a tube current of 60 mA and a voltage of 40 kV, Atomic absorption spectrometer (AAS) of Thermo S-series, Gravimetric and volumetric method. The mineral compositions of the sample was studied by X-ray diffraction (XRD) using a Bruker diffractometer model D8 discover with Cu Kα radiation at a current of 40 mA and a voltage of 40 kV. The XRD pattern was studied over 2θ value from 6^0 to 90° at a scan speed of 1.2°/min while maintaining an inert gas atmosphere to identify different phases present in the sample. Thermo-gravimetric (TG) and differential thermal (DTA) analysis was performed in an argon atmosphere from 25 °C to 1000 °C at heating rate of 10 °C min^{-1} by using LECO 701. A Nova NanoSEM 430 UHR scanning electron microscope (SEM) equipped with energy dispersive

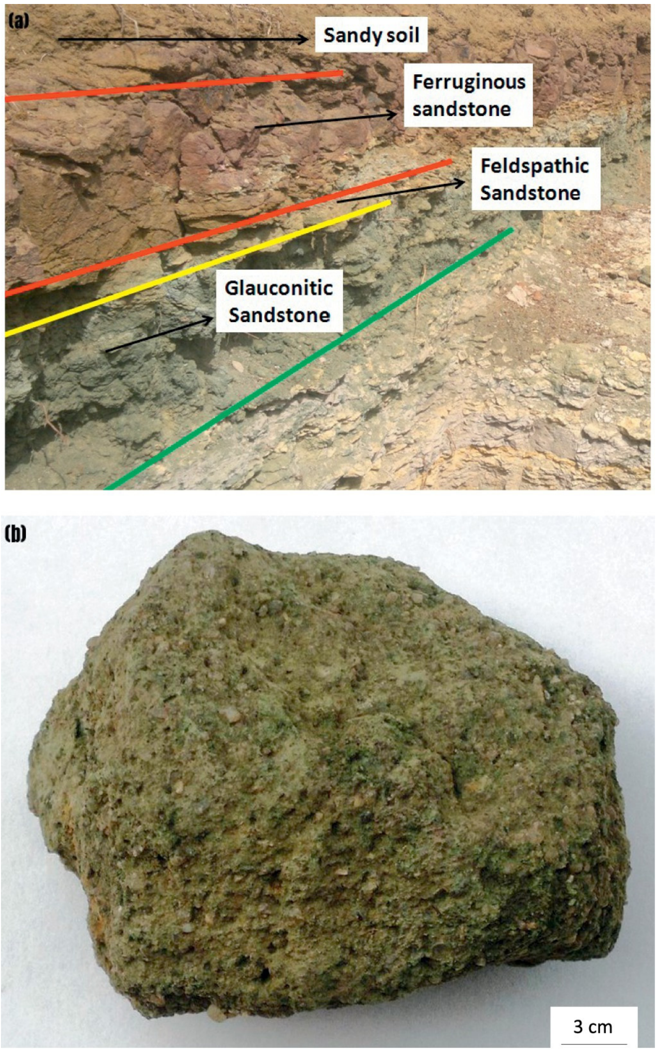

Fig. 1. Trench for sample collection (a) collected sample (b).

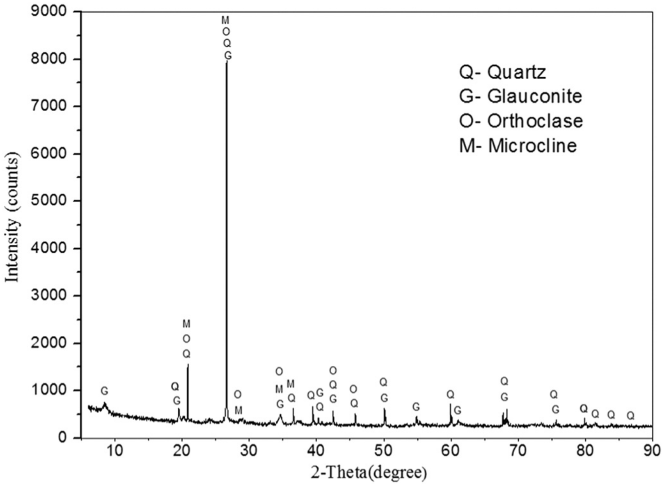

Fig. 2. XRD pattern of glauconitic sandstone.