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Micellar mediated selective leaching of manganese nodule in high temperature sulfuric acid medium

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The present study evaluates the possibility of selective leaching of manganese from complex, manganese and iron oxy-hydroxide based sea bed nodule utilising micelles in high temperature acid dissolution process. Application of surfactants during acid leaching of manganese nodules are described based on results from leaching studies. The factors that affected the sulfuric acid leaching of the manganese nodules in the presence of various surfactants were investigated. The effect of anionic (SDS-Sodium Dodecyl Sulphate), cationic (CTAB-Cetyl Trimethyl Ammonium Bromide) and nonionic (Triton-X 100) surfactant on the various metals extraction with respect to sulfuric acid concentration, temperature, type of surfactants and surfactant concentration is reported. Among them, CTAB showed highest improvement in the recovery of Cu, Ni, Co, Zn and Mn. Iron, aluminium, and silica were removed effectively through the present approach of high temperature sulfuric acid leaching route assisted by surfactant. Increasing the temperature of the medium has significant impact in the selective leaching of Mn, Cu, Ni and Co. The optimum conditions established for maximum metal extraction are: pulp density 10%, time 2 h, temperature 160 °C, sulfuric acid 5.0% (*v*/*v*) and at critical micellar concentration of CTAB. Under these conditions, recovery of Mn was 99% along with the (˜99%) recovery of Cu, Co, and Ni. The leached residues were analysed and their phase and morphologies were included herein. The present process may find application of separation of manganese from iron and aluminium at high temperature during various hydrometallurgical treatment of manganese based ores.

1. Introduction

A number of surfactants are extensively used in mining, petroleum, industrial, agriculture, food, cosmetics, and pharmaceutical (Li and Fang, 2002) processes due to reduction of the surface or interface tension. Surfactants are also beneficial as dispersants to increase extraction rates during leaching of metals and non-metals (Owusu et al., 1995; Karavasteva, 2001; Fan et al., 2004; Tan et al., 2004; Tan et al., 2014; Zhuo et al., 2009; Mohammad et al., 2012; Okoliegbe and Agarry, 2012; Samanta et al., 2013). It has been established from the published literature that surfactants are beneficial during extraction of uranium from low permeable sandstone uranium deposits and sulphur containing ores. Recently, addition of the surfactant during wet grinding of roast-reduced polymetallic sea nodule pellets was found to be beneficial in improving recovery of cobalt from polymetallic sea nodules in NH_3–$(NH_4)_2CO_3$ leaching process (Mishra et al., 2011). Nodules are good alternative resources of Mn, other important transition metals (Meylan, 1968; Bezrukov and Andrushchenko, 1972; Mukhopadhayay et al., 2003) and some rare earth elements (Heina et al., 2013; Mohwinkel et al., 2014; Randhawa et al., 2015). The metals such as Cu, Ni, Co and Mn are present in the form of oxides or hydroxides (Acharya et al., 1999; Ghosh et al., 2008). Voluminous work has been reported for recovery and processing of nodules by various metallurgical routes (Sen, 1999; Randhawa et al., 2015). Extraction of metal values from low and medium grade ores is also attracting the industries such as steel, nonferrous metallurgy, dry cells or batteries and chemical industries (Hariprasad et al., 2007; Xue et al., 2014; Jiang et al., 2004). The extraction of manganese from these resources should be carried out under reducing conditions as manganese dioxide ores are quite stable in acidic medium. Researchers have studied different routes for the recovery of Mn containing ores via roasting process (Sharma, 1992; Sahoo and Rao, 1989), reductive acid leaching using various reducing agents (Hariprasad et al., 2007; Xue et al., 2014; Cheng et al., 2009; Abbruzzese, 1987; Das et al., 1982, 2012; Ismail et al., 2004; Sahoo et al., 2001; Tang et al., 2014) in aqueous methanol-sulfuric acid medium (Momade and Momade, 1999) and also in sulfuric acid medium (Su et al., 2008; Tian et al., 2010). Efficacy of the extraction of metal values depends on the reducing atmosphere, leaching temperatures and acid concentrations (See Table 1). Thus continuous research is going on to develop suitable flowsheets for improving the leaching efficiencies of the valuable metal values along with the rejection of iron. In the present work, we have attempted to find one such solution for the recovery of metal values from sea bed nodules in absence of reductant

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Table 1
% extraction of metal values from manganese nodule leaching under various conditions.

Material	Reducing agent	Temperature	Result	Reference
Ground nodule + H_2SO_4	Hydroxyl benzene	Ambient	Mn, Cu, Ni and Co increased to 97%, 95%, 94% and 98%, respectively with 90% of Fe	Zhang et al. (2001)
H_2SO_4 + sea nodule	Sawdust	90 °C	–	Hariprasad et al. (2007)
Sulphuric acid solution	Oxalic acid	~85 °C	98.4% Mn	Sahoo et al. (2001))
H_2SO_4 + sea nodule	Cane molasses	90 °C	97.0% for Mn, whereas 21.5% for Al and 32.4% for Fe	Su et al. (2008)
MnO_2 and H_2SO_4 conc.	Glucose	90 °C	–	Furlani et al. (2006)
Manganese oxide ore + H_2SO_4	Methanol	150 and 170 °C	98% Mn	Momade et al. (1999)
H_2SO_4 + MnO_2	Sawdust $(C_6H_{10}O_5)_n$ or Lactose $(C_{12}H_{22}O_{11})_n$	70 °C	92.5% Mn recovery	Ismail et al. (2004)
MnO_2 + H_2SO_4	$FeSO_4$	90 °C	99% of manganese recovery	Das et al. (1982)
Sea based manganese ores + H_2SO_4	NH_3 NH_2 H_2SO_4 (hydrazine sulphate)	110 °C	96.9% Mn, 85.25% Cu, 92.58% Ni and 76.5% Co extraction	Hariprasad et al. (2013)
Sea based manganese ores + H_2SO_4	Oxygen pressure to 100 psig	200 °C	Recovery of Mn,Ni,Co	Han and Fuerstenau (1975)
Sea based manganese ores + H_2SO_4	Oxygen partial pressure at 0.55 MPa	150 °C	Extraction of copper, nickel, cobalt and manganese were 77, 99.8, 88 and 99.8% respectively	Anand et al. (1988)
Manganese nodules	$FeSO_4$–H_2SO_4–H_2O	90 °C	90% of Ni, Cu and Mn extracted	Vu et al. (2005)
Manganese nodules	SO_2 –H_2SO_4 – $(NH_4)_2$ $SO)_4$	263 K	88.5% Cu, 99.8% Ni, 91.8% Co, 97.8% Zn, 99.6% Mn with iron extraction of 2.48%	Acharya et al. (1999)
Roasted Sea nodules + surfactant	NH_3–$(NH_4)_2CO_3$	at room temperature (~25 °C)	94.80% Cu, 94.0% Ni and 80.8% Co	Mishra et al. (2011)

using various surfactants. Mishra et al. (Mishra et al., 2011) has showed that using anionic surfactant in ammoniacal process of nodules, the recovery of cobalt can be improved. However no work has been reported so far on the role of surfactants during the acid leaching of nodules. In the present study, cationic, anionic and neutral surfactants are used in sulfuric acid medium for the recovery of manganese and other metals due to their interaction with solute through electrostatic force or hydrogen bond interaction, or by the self-organization process. The present work is thus an attempt to leach Cu, Ni, Co, and Mn while maximizing the rejection of iron to the residue. Surfactant media may offer a cleaner alternative to more traditional methods.

2. Materials & methods

Manganese nodules collected from the Central Indian Ocean Basin by CSIR-NIO, Goa, were air-dried and ground. The nodule samples were crushed, ground and sieved to obtain 100% -150 mesh B.S.S fraction (<100 μm). Cetyltrimethylammonium bromide ($C_{19}H_{42}BrN$) and sulfuric acid from Merck, India were used without further purification. Double distilled water was used in all the experiments. Electrokinetic measurements of manganese nodule particles, both in the presence and absence of surfactants, were performed under room temperature in a particle size analyser (Microtrac–Zetatrac). The pH of the suspensions was adjusted with the addition of 0.01 M HCl or NaOH. Leaching experiments were carried out in 2 L Parr autoclave (Model 4542) made of 316 stainless steel. The reactor has provisions for gas inlet/outlet, sampling and internal cooling. For mixing, two six bladed turbine impellers with downward thrust were attached to the shaft. Temperature was controlled through a PID controller with digital read-out for temperature, pressure and agitation speed. Initially, the required amount of concentrated H_2SO_4 was mixed with the weighed amount of surfactant and mixed thoroughly, followed by addition of manganese nodule. The whole mass was then transferred to the reactor under required temperature and time period. After 2 h, the slurry was cooled, filtered and the filtrate was analysed for metal ions using atomic adsorption spectrophotometer (Perkin Elmer AA 200). Experiments were carried out in triplicate in order to estimate the error. The average values of percent extraction of metal values of three experiments were considered for graphical representation. The crystal structures of the Mn nodule and leach residues were studied by X-ray diffraction (XRD) using an automated XRD Phillips Powder Diffractometer, Japan (Model PAN ANALYTICAL PW 1830) in the range of 5–80° (2θ) at a scanning rate of 2°/min with Copper target. Morphology were identified with Supra 55; Zeiss (Germany Make) with a resolution of 1.0 nm at 30 kV and equipped with 20 mm^2 Oxford EDS detector.

3. Results and discussion

3.1. Digestion studies (elemental analysis) and XRD analysis of the manganese nodules

Required amount of sieved manganese nodules were digested using combination of various acids such as H_2SO_4, HCl, HNO_3 and $HClO_4$. The filtrates were used for elemental analysis of Mn, Cu, Ni, Co, Zn, Mo and Al and the acid insoluble residues mostly contain silica. The average content of valuable metals in the nodules were estimated to be 18.88% Mn, 0.98% Cu, 5.28% Fe, 1.17% Ni, 0.09% Co, 0.078% Zn, 1.78% Al, 0.056% Mo along with 22.5% acid insoluble residue. The different crystalline phases of the sample have been identified from the XRD patterns in Fig. 1. The peak locations and their corresponding relative intensities for the phases were cited from the Joint Committee on Powder Diffraction Standards (JCPDS) database. The peaks located at two-theta values of 8.97, 12.29, 18.11, 27.96 and 36.69° corresponded to the planes of the todorokite phase (ICDD00-012-0183) and the peaks located at two-theta values of 20.84, 26.69, 50.27, 55.14° corresponded to the planes of the quartz phase (01-087-2096) respectively. The mineralogy of Mn nodules had also been reported earlier as todorokite and subordinate δ-MnO_2 (Nayak et al., 2011). The other minor cationic species such as copper, cobalt, nickel and rare earth metals were disseminated in the oxide matrix through sorption process. Thus, the phases of nodule were described by many authors as hydrous oxide of Mn and Fe.

3.2. Sulfuric acid leaching studies of manganese nodules

3.2.1. Effect of the nature of surfactant on the metal extraction

To study the effect of nature of surfactant on the metal extraction values, cationic, anionic, and non-ionic surfactants like CTAB, SDS, Triton X-100 and Tween-80 were used under similar two experimental conditions. Amount of the surfactants were added to the acidic leaching reagent as per their critical micelle concentration (CMC) values. CMC values for CTAB, Triton X-100, SDS and Tween-80 were found to be 0.92, 0.24, 8.2 and 0.012 mM under room temperature respectively. In