Minerals Engineering 115 (2018) 106–116

Contents lists available at ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

Efficient extraction of copper and zinc from seafloor massive sulphide rock samples from the Loki's Castle area at the Arctic Mid-Ocean Ridge

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A R T I C L E   I N F O

Keywords:
Seafloor massive sulphide
Copper
Zinc
Leaching
Extraction
Nitric acid
Deep sea mining
Marine minerals

A B S T R A C T

Seafloor massive sulphide (SMS) deposits have been identified as important marine metal resources for the future. However, literature on the recovery/extraction of metals from SMS is currently limited, and to date, no research has been published on the processing of SMS from the active hydrothermal vent field at the Arctic Mid-Ocean Ridge. In this paper extraction of copper and zinc, as economically important metals, from the seafloor massive sulphide rock samples from the Loki's Castle area at the Arctic Mid-Ocean Ridge was investigated during nitric acid leaching. The results presented are of the various leaching experiments conducted under different conditions to optimise the extraction of copper and zinc. The mineralogical analysis indicated that the main copper and zinc bearing minerals were chalcopyrite and sphalerite, respectively. It was shown that the leaching efficiency and extraction of copper and zinc can be controlled mainly by temperature and acid concentration. The elemental composition and mineralogical data indicated that 95% of copper and zinc bearing minerals were leached out after 3 h, at the solid-to-liquid ratio of 1:10, temperature of 90 °C and acid concentration of 10%.

1. Introduction

1.1. Geological setting of seafloor massive sulphide deposits

Rapidly increasing per capita demand for copper (Singer, 2017) in developing countries has served to increase the requirements for geologically diverse base metal resources, and recent research in the deep-sea environment has identified areas of mineralisation that may become economically important for society (Hannington et al., 2001). Marine mineral resources can be classified based on the sources of their origin, i.e. (*i*) terrestrial, (*ii*) combined terrestrial and deep ocean and (*iii*) ocean basin resources (Arbab et al., 2015). The characteristics and importance of marine mineral deposits from terrestrial (e.g. heavy metal elements) as well as combined terrestrial and deep ocean sources (e.g. polymetallic nodules and cobalt-rich ferromanganese crusts), have been well described (Morgan, 2000; White et al., 2011).

Marine minerals from ocean basin sources have their origin in the ocean floor. They are derived from fluid/rock interaction within the ocean crust and precipitation of minerals therein. The most important ocean deposits are (*i*) metalliferous sediments, and (*ii*) seafloor massive sulphides (SMS). The first SMS were discovered at the crust of East Pacific Rise in 1978 (Francheteau et al., 1979). Since 1979, SMS deposits have been known to occur at water depths up to 3700 m in a variety of tectonic settings at the modern seafloor including mid-ocean ridges, back-arc rifts and seamounts (Herzig et al., 2002). SMS-style mineralisation shares many characteristics with classic volcanogenic massive sulphide (VMS) deposits and may be considered as modern analogues of this important deposit type, which has important economic implications.

Hydrothermal vent fields with multiple fluid channels culminating in black smokers (chimneys) mostly consist of pyrite (FeS_2) and chalcopyrite ($CuFeS_2$) together with pyrrhotite ($Fe_{1-x}S$, where x ranges from 0.0 to 0.2), isocubanite ($CuFe_2S_3$) and bornite (Cu_5FeS_4) with gangue material such as barite ($BaSO_4$) and silica (SiO_2) (Herzig et al., 2002; Pedersen et al., 2010). The mineralogical compositions of Back-Arc and Mid-Ocean Ridge SMS deposits are contrasted in Table 1.

1.2. Processing methods for SMS material

Many processes have been investigated in order to assess the best one, which extracts economically important metals such as nickel, copper, cobalt and manganese from seafloor nodules and crusts. There

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http://dx.doi.org/10.1016/j.mineng.2017.10.015
Received 31 May 2017; Received in revised form 9 October 2017; Accepted 16 October 2017
Available online 06 November 2017
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Table 1
Mineralogical composition of SMS deposits (Herzig et al., 2002).

	Back-arc deposits	Mid-ocean ridge deposits
Fe-sulphides	Pyrite, marcasite, pyrrhotite	Pyrite, marcasite, pyrrhotite
Zn-sulphides	Sphalerite, wurtzite	Sphalerite, wurtzite
Cu-sulphides	Chalcopyrite, isocubanite	Chalcopyrite, isocubanite
Silicates	Amorphous silica	Amorphous silica
Sulphates	Anhydrite, barite	Anhydrite, barite
Pb-sulphides	Galena, sulphosalts	
As-sulphides	Orpiment, realgar	
Cu-As-Sb-sulphides	Tennantite, tetrahedrite	
Native metals	Gold	

are two main processing technologies: leaching, in either hydrochloric/sulphuric/nitric acid or ammonia solutions, and smelting (Fuerstenau and Han, 1983; Jana et al., 1990; Chung, 1996; Niinae et al., 1996; Charewicz et al., 2001; Senanayake, 2011). Hydrometallurgical processing has become an important aspect in the recovery of valuable metals since it meets industrial requirements in terms of cost and technical effectiveness, ease of operation, lower emission of gases to the atmosphere, and ability to be scaled-up (Pasad and Pandey, 1998; Olubambi and Potgieter, 2009; Chmielewski, 2015). However, literature on the recovery/extraction of copper and zinc from SMS is currently limited, and to date, no research has been published on processing of SMS from the Loki's Castle area at the Arctic Mid-Ocean Ridge. In this paper, extraction of copper and zinc from the seafloor massive sulphide rock samples from Loki's Castle during nitric acid leaching is investigated, as maximising the effectiveness of metal recovery from SMS ores is critical in development of such mineral showings in to future ore reserves.

Although the use of nitric acid as a leaching agent (lixiviant) in industry is limited due to its high price in comparison to sulphuric acid (H_2SO_4), nitric acid is a strong oxidation agent and offers excellent potential for achieving very high levels of metal recoveries. Moreover, leaching of sulphides in the presence of nitric acid does not require the use of additional oxidants such as oxygen and ferric ions (Fe^{3+}), and the leaching time is faster in comparison to sulphuric acid, which will reduce the operational costs. Despite the initial expense, almost all of the nitric acid can be recycled and noxious gases can be captured, reducing the raw material costs (Ma et al., 2013).

2. Materials and methods

2.1. Materials

Various rock samples from the SMS ore from the Loki's Castle hydrothermal vent field at the Arctic Mid-Ocean Ridge (Fig. 1) were investigated. Loki's Castle is a site of known active hydrothermal venting as first described by Pedersen et al. (2010), where sulphide-carrying fluids are expelled from chimneys, forming black smokers. The vent field, occurring at the junction of the Mohn's and Knipovich Ridges in the Arctic Ocean, consists of five chimneys located on the top of two mounds at approximately 2400 m depth (Pedersen et al., 2010).

The samples used in the leaching tests were collected during the MarMine cruise in 2016 (Ludvigsen et al., 2016). The location and areas of operation are shown in Fig. 1. The collected rock samples were bagged, flushed with nitrogen and vacuum sealed to prevent oxidation, and then stored in a fridge at +4 °C. This paper utilises only a small but representative range of available sample material, as an initial investigation into the mineral extraction potential of SMS deposits.

Prior to tests, the samples were unpacked and dried at room temperature. The chemical composition of each sample was determined by X-ray fluorescence (XRF). Small amounts of different parts of samples were collected and crushed either by an agate hand mortar or steel jaw and roller crushers. Table 2 shows the elemental composition of investigated rock samples. It can be clearly seen that the samples varied in composition. Based on XRF data the individual particles were classified as a feed (F), a middling (M) and a waste (W). Only samples with copper and zinc content of at least 0.5 and 1.0%, respectively, were used in the leaching experiments, i.e. feed (LCA11) and middling

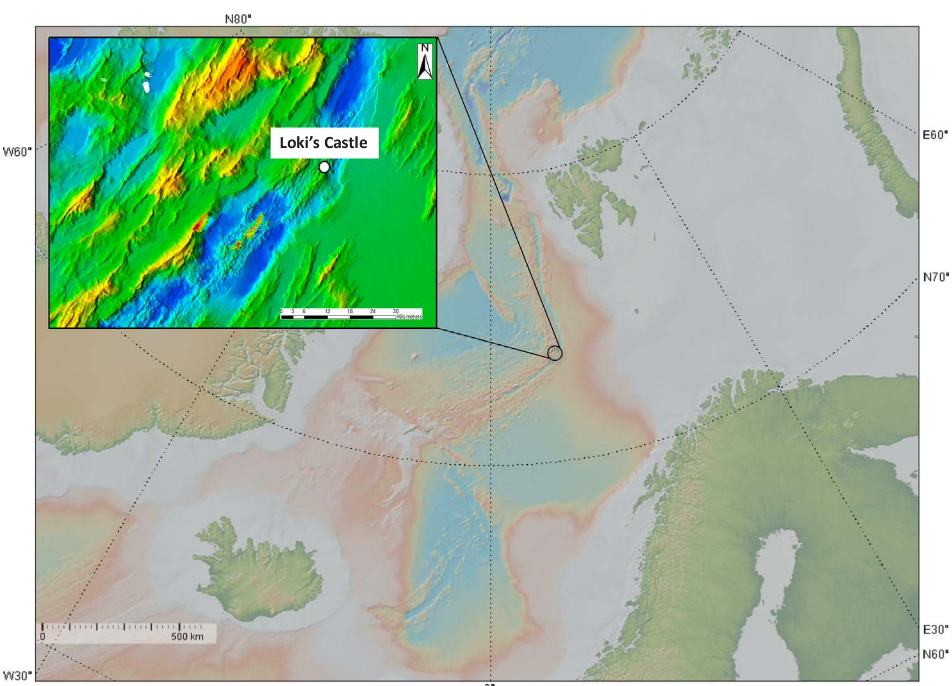

Fig. 1. Loki's Castle hydrothermal vent field (the northern part of Mohn's Ridge) at the Arctic Mid-Ocean Ridge (inset shows operation area) (Ludvigsen et al., 2016).

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