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Reactive Oxygen Species in Novel Hydrometallurgical Processes

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Abstract

Novel hydrometallurgical processes based on the reactive oxygen species (ROS) for high-efficiency treatment of refractory amphoteric metal-containing mineral resources have been developed. Due to the strong oxidizing capacity, ROS-rich sub-molten salt media significantly decrease the reaction condition and increase the extraction ratio in comparison of traditional methods. New concept and insight of ROS intensification and ROS electrochemical modulation has been proposed recently.

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Introduction

As a typical technique for recovery of metals from their ores, concentrates and secondary resources, modern hydrometallurgy has been developed from the end of 19th century [1]. Efficient oxidative dissolution process is a crucial procedure for the comprehensive utilization of the valuable metals. With the shortages and grade decreasing of global mineral resources, novel high-efficiency hydrometallurgical processes are proposed in recent years. A novel concept of reactive oxygen species (ROS) in hydrometallurgy process was emerged due to its high oxidative stress for the dissolution of mineral or ores [2].

ROS are chemically reactive species containing oxygen, such as peroxides (O_2^{2-}), superoxide (O_2^-), hydrogen peroxide (H_2O_2) and hydroxyl radical (•OH). It was firstly developed in biological field, which is formed as a natural byproduct or metabolite of oxygen in cell [3]. In some specific circumstance such as illumination or thermal radiation, ROS in the cell would increase dramatically and result in severe cell damage according to the high-level oxidizing ability. On the contrary, modulation of ROS preciously under the microenvironment for the attack of tumor stem cells could be an effective cancer therapy. It can also be introduced to the field of manufacturing industry, chemical engineering and hydrometallurgy.

Based on the principles of cleaner production in hydrometallurgy, sub-molten salt (SMS) technology has been developed by Institute of Process Engineering, Chinese Academy of Sciences (IPE, CAS) [4-5]. It is confirmed that ROS plays the major role in the sub-molten salt medium. Compared with traditional roasting or leaching methods, variously kind of amphoteric metal can be extracted from the minerals with lower temperature, high extraction ratio and less hazardous waste through the reinforcement of ROS in SMS media. Furthermore, ROS modulation techniques by electrochemical methods have been confirmed as an effective route recently.

Reactive Oxygen Species in Sub-molten Salt Technology

Sub-molten salt, a highly concentrated alkali metal hydroxide solution with high chemical reactivity and high ionic activity, is a novel reaction media in hydrometallurgy. High reactivity of SMS is due to large quantity of ROS existed in the media. Fundamental understanding of ROS in alkaline media has been approved that SMS is an ideal carrier for the ROS (mainly consists O^{2-}, O_2^-, O_2^{2-}) originated from chemical intensifying effect [6].

Quantitative detection of ROS in alkaline media can be achieved by using UV-vis method based on fluorescent probes or chromogenic reagents [7]. Media concentration, reaction temperature, pressure and reaction time have a significant impact on the ROS concentration. Besides, with the rapid development of electrode preparation and nanomaterial fabrication, the determination of ROS by electrochemical method is also a good choice.

Refractory amphoteric minerals, such as chromium (Cr), vanadium (V) and manganese (Mn) can be oxidative decomposed in alkaline condition, especially in SMS media, with relatively high utilization ratio and mild condition in comparison to traditional methods [8-13]. Till now, based on this technology, industrial production lines for the treatment of chromite, vanadium slag and other minerals have been successfully built or put into production.

The mineral lattice could be efficiently attacked by the ROS in the media. The O^{2-} generated from OH^- decomposition and O_2^-, O_2^{2-} and other derivative generated from oxygen reduction can facilitate and activate the refractory amphoteric mineral dissolution process. Compared with traditional lime-free roasting method in rotary hearth furnace (1200°C), liquid-phase oxidation for the production of chromate salts by the pressure leaching in KOH sub-molten salt, $KOH\text{-}KNO_3$ binary sub-molten salt and $NaOH\text{-}NaNO_3$ binary sub-molten salt was presented [8-11]. Much higher Cr recovery ratio (nearly 100%) and less toxic Cr(VI)-containing residue (only 20% of the traditional process) are obtained by this novel hydrometallurgical process as shown in Figure 1. Due to the stable ROS in the KOH sub-molten salt and $NaOH\text{-}NaNO_3$ binary sub-molten salt, vanadium

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and chromium in the vanadium slag can be synchronously extracted [12]. The essence of this method is to oxidize the low valance state chromium or vanadium in the refractory chromium-vanadium spinel to water soluble salts.

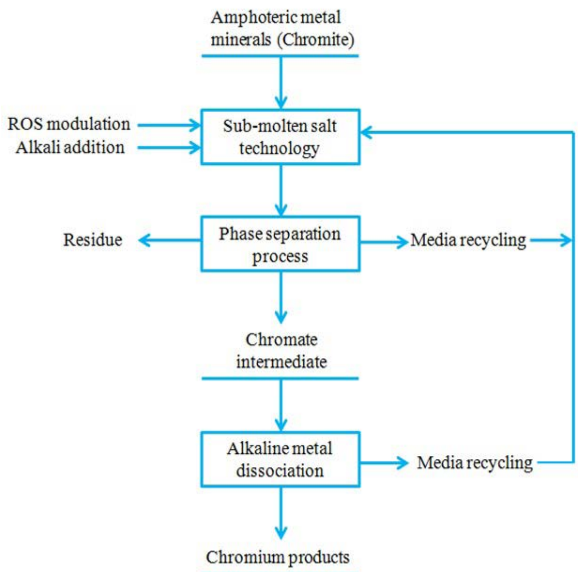

Figure 1: Flow chart of typical sub-molten salt technology.

Reactive Oxygen Species Modulation by Electrochemical Methods

In order to enhance the mass transfer of alkaline media and promote the formation of ROS, it is essential to investigate how to modulate ROS by novel techniques. The main superiority of electrochemical methods is environmental compatibility by directly consuming the "clean reagent" of electron, promoting its potential application and receiving great attention with the advantage of operation versatility, controlled accurately and amenability of automation. In such a situation, the electrochemical technology for the ROS modulation in alkaline media was proposed, offering a promising pathway to further intensify the hydrometallurgical process (Figure 2) [14].

Novel electrochemical amphoteric metal oxidation strategy by in-situ generated ROS on the cathode surface was developed. ROS (HO_2^-) was firstly produced from two-electron-pathway oxygen reduction. Hydroxyl radicals are subsequently generated from the electro-Fenton or electro-Fenton-like reaction in this electrocatalytic process. It is reported that synchronously oxidation of chromium and vanadium was successfully achieved in single-compartment electrolytic cell [15]. As shown in Eq.(1)-(2), hydroxyl radicals are induced from the electro-Fenton-like reaction between Cr and HO_2^-. The oxidative conversion ratio of Cr(III) and V(III) could greatly enhanced with the synergistic effect of ROS modulated by electrochemical condition. This novel electrochemical intensification approach may serve for the treatment of chromium-containing, vanadium-containing and other refractory minerals and solid wastes.

$$Cr(III) + HO_2^- \rightarrow Cr(VI) + \bullet OH + OH^- \quad (1)$$

$$V(III) + \bullet OH + OH^- \rightarrow V(V) + H_2O \quad (2)$$

Summary

Based on the above discussions, ROS, as a type of clean and high capability oxidizing agent, has been applied in novel hydrometallurgical processes. In sub-molten salt technology, large amount of stable ROS (O^{2-}, O_2^-, O_2^{2-}) can be aroused from the strong alkaline media. With the intensify effect of ROS, variously kind of amphoteric metal can be efficient extracted from the minerals or solid wastes under relatively mild conditions. According to the investigation of ROS electrochemical modulation strategy, HO_2^- and hydroxyl radical play a key role in the oxidative dissolution process, suggesting a promising potential for the industrial applications.

Competing Interests

The authors declare that they have no competing interests.

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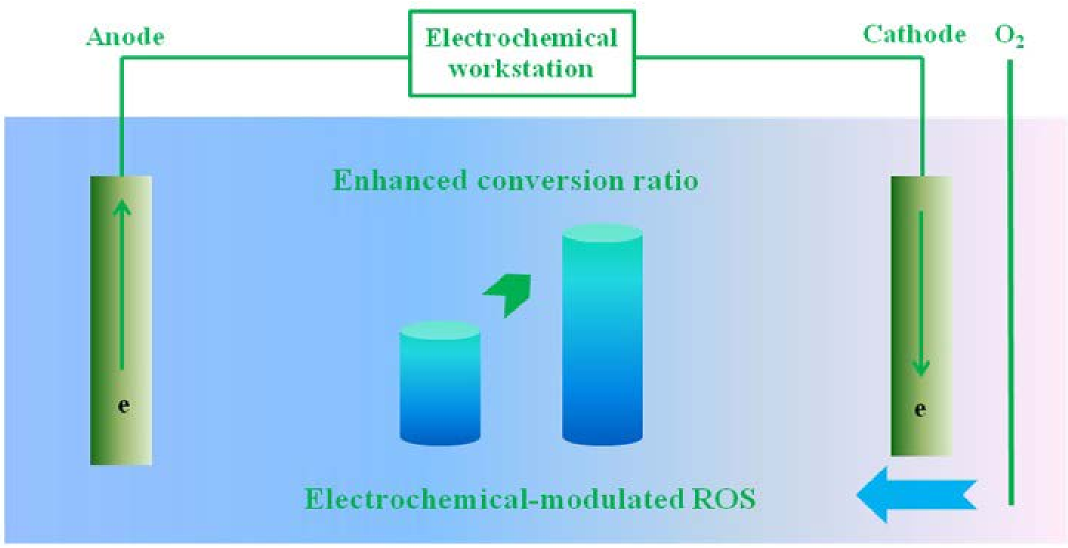

Figure 2: Reactive oxygen species modulated by electrochemical techniques.

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