SUB-MOLTEN SALT ENVIRONMENTALLY BENIGN TECHNOLOGY

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Introduction

The global industrial growth has spawned environmental concerns on a global scale. As two challenges of the sustainable development, eco-efficiency and ecosystem pressure have widely raised public awareness throughout the world (Jansen, 2003). In some developing countries, the industrialization has stepped into the peak phase of resource consumption. Industrial pollution and eco-environmental injury will become recognized problems impeding the progress of global economy and sustainable development. The key issue in establishing the sustainable economic pattern is the green upgrading of the huge resource-processing systems resulted from process industries (Zhang, 2001). It has become the main goal of global economic revolution to achieve the economic growth with the least resource-environment cost, maintain the harmoniousness of the eco-system, guarantee the effective eco-utilization of natural resources, and build up an evolving ecological economic pattern. Thereby, a highly challenging strategic innovation direction has been pointed out to the scientists at the same time.

Similar with other developing countries, China’s mineral processing contributes greatly to its environmental pollution. With the objective of improving resource utilization efficiency and eliminating environmental pollution at the source, an emerging technology, so-called Sub-Molten Salt (SMS) technology, has been developed by the Institute of Process Engineering, Chinese Academy of Sciences. The SMS technology has the potentials to processing many amphoteric metal resources including chromite, bauxite, and ilmenite. In this paper, the definition of SMS media will be interpreted and the advantage of SMS media in hydrometallurgical process will be elaborately discussed. Then the application of the SMS media in manufacturing chromium compounds, as well as the green hydrometallurgical platform on the basis of the SMS media, will be introduced.

Conception of Sub-Molten Salt (SMS) Unconventional Media

Definition of SMS Media

For aqueous electrolyte solution, solution chemistry and thermodynamic investigation covers usually the low concentration range. When we talk to aqueous electrolyte solution, we commonly refer to aqueous electrolyte solution with low concentration. Physical chemistry research on molten salt has become a popular topic for metallurgy and electrochemistry. However, the solution region between molten salt and common electrolyte aqueous solution has rarely been investigated so far due to the difficulty in experimental measurement and theoretical model construction. The application of highly concentrated aqueous electrolyte solution to hydrometallurgical process has achieved a great progress in our work. It was found that in the high concentration region, the physical chemistry properties of electrolyte aqueous solution becomes remarkably different. As shown in Fig. 1, the highly concentrated aqueous electrolyte solution region was called as SMS region in our work.

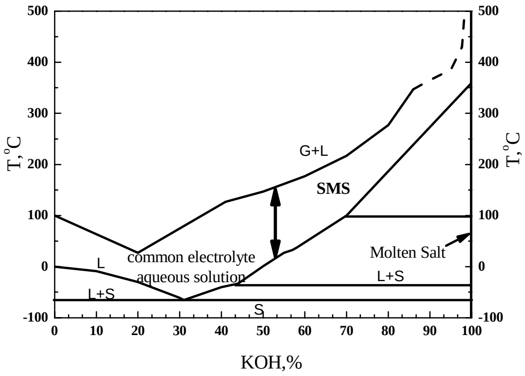


Fig. 1. SMS Region of Aqueous Electrolyte Solution

The SMS unconventional media (Zhang, 2007) was defined as a kind of controllable ionized media of highly concentrated multi-component system with alkali metal hydroxides. It is capable of providing highly active oxygen anion and thereby intensifying reaction and mass transfer process. Taking KOH SMS as an example, in aqueous solution with the presence of oxygen, KOH will be ionized into potassium cation K^+ and hydroxide anion OH^- (Equation (1)). The hydroxide anion OH^- will further be decomposed into water molecule H_2O and oxygen anion O^{2-} (Equation (2)). By combining with oxygen molecule, the oxygen anion O_3^{2-} becomes even more active (Equation (3)).

$$KOH \rightarrow K^+ + OH^- \tag{1}$$

$$2OH^- \rightarrow H_2O + O^{2-} \tag{2}$$

$$O^{2-} + O_2 \rightarrow O_3^{2-} \tag{3}$$

Physical-chemistry Characteristics of SMS Media

The physical-chemistry characteristics of SMS media include the following four aspects. The first is ***high boiling point and low vapor pressure***. For SMS media, a higher solute concentration leads to a higher boiling point, as shown in Fig. 2. Therefore, under the same reaction temperature, the vapor pressure of SMS media is lower than common electrolyte aqueous solution with low concentration. In other words, the SMS media enables a higher reaction temperature under atmospheric pressure.

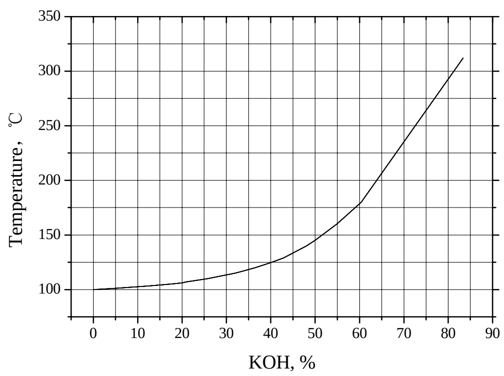


Fig. 2. Relationship of Boiling Point and Concentration for Aqueous KOH Solution

The second characteristic of SMS media is ***high mean ion activity coefficient***. As shown in Fig. 3, in low concentration range, the mean ion activity coefficient increases slightly with the increasing of mole fraction of KOH. However, in high concentration range as well as SMS region, the mean ion activity coefficient increases remarkably with the increasing of mole fraction of KOH.

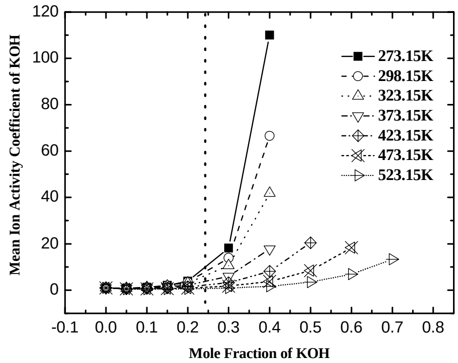


Fig. 3. Relationship of Mean Ion Activity Coefficient and Mole Fraction for Aqueous KOH Solution under Different Temperatures (Data from Li, 1996)

The third characteristic of SMS media is ***excellent performance in flow and transfer***. For SMS media, when operating under higher temperature, its viscosity becomes lower and it will help to improve the fluidity and mass transfer of the aqueous system. The last characteristic is ***easy process control and quantitative adjustment***. As ionic solvent for hydrometallurgical processes, the SMS media achieves the quantitative controlling and system optimization during the process of reaction.

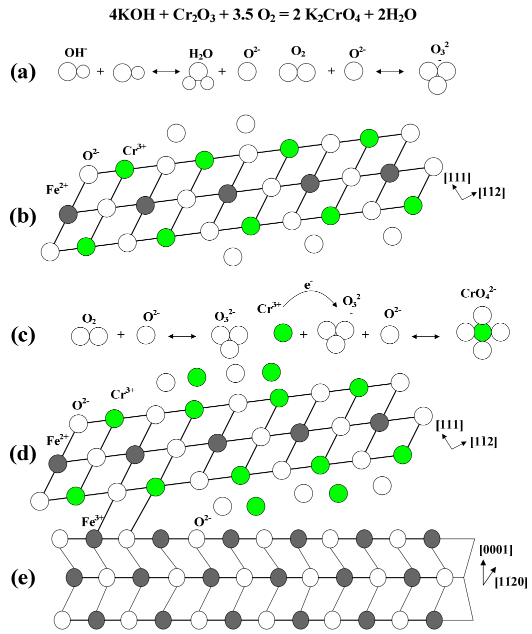
Reaction Intensification Effect of SMS Media

In a typical hydrometallurgical process, some components, including the target component, in mineral ore particles usually become soluble and are dissolved into the aqueous solution system with the interaction of the reaction media under certain temperature, pressure, pH value, etc. The SMS media exhibits many advantages in hydrometallurgical process. The physical-chemistry characteristics mentioned above help to achieve a more environmentally benign process in industrial operation with high reaction temperature but low vapor pressure, excellent fluidity, high reaction activity, and easy control. In fact, the presence of SMS media makes the decomposition of mineral ore particles more efficient and easy. Fig. 4 illustrated the decomposition process of chromite ore in SMS media of KOH.

The high mean ion activity coefficient and high soluble oxygen anion concentration enables to effectively facilitate the transfer of the oxygen anion in the mineral surface, greatly enhance the abnormal change of the mineral surface structure, essentially intensify the decomposition of mineral particles, and remarkably increase the conversion of target component to near 100 percent.

Separation Facilitation Effect of SMS Media

As highly concentrated electrolyte aqueous solution, the SMS media helps to facilitate the separation of target products from the multi-component system due to the salting-out effect of different electrolyte solutes. With reference to the phase equilibrium data and phase diagram, the clean coupling of reaction and separation can be achieved through adjusting the concentrations of different solutes in the aqueous system, as shown in Fig. 5.



(a) dissolution of oxygen and creation of oxygen anion; (b) main body of chromite ore particle and $FeO{\cdot}Cr_2O_3$ crystal; (c) oxidation of trivalent chromium ion; (d) $FeO{\cdot}Cr_2O_3$ crystal structure destroy, Cr^{3+} dissociation, and product dissociation; (e) creation of Fe_2O_3 product layer.

Fig. 4. Decomposition Process of Chromite Ore in SMS Media

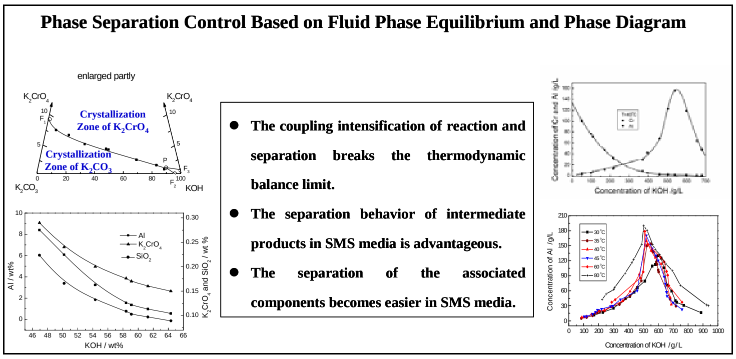


Fig. 5. Phase Separation Behavior of Multiple Components in SMS Media

Case Study: Hydrometallurgical Processing of Chromite with SMS Media

General Background

Chromium compounds are essential to many industries, but their manufacturing process is usually a major source of pollution. In traditional manufacturing process that uses oxidation roasting at high temperature, the utilization efficiency of resources and energy is quite low. Chromate plants discharge large amounts of chromium-containing residues, dusts, and waste gases. Chromium-containing residues create serious pollution problems that threaten groundwater, rivers, and marine areas (Walawska, 2001). By using the SMS media, an environmentally benign hydrometallurgical process of chromite was achieved. The resource utilization efficiency was greatly improved, the energy consumption was remarkably decreased, and the source reduction and zero emission of chromium containing residue was achieved (Zhang, 2005).

Raw Materials Substitution

As illustrated in Fig. 6, the raw materials of the green process with SMS media include only chromite ore, K^+ or Na^+ in form of KOH or NaOH SMS respectively, and air. However, in traditional process, inert additives and sulfuric acid are also employed. The traditional process discharges toxic wastes including Cr-containing residue and Cr-containing Glauber's salt, leading to serious environmental problems. Correspondingly in the green SMS process, the comprehensive utilization of chromite resources is achieved. The ferrite-enriched chromium residue can be used to manufacture desulphurization agent byproduct, and zero emission of Cr-containing residue is achieved.

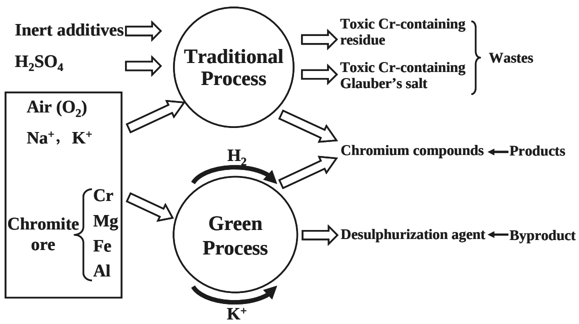


Fig. 6. Raw Materials Substitution in the Green Process with SMS Media

Reaction Mode Innovation

The essence of the green SMS process is that traditional oxidation roasting of chromite ore with sodium carbonate at 1200°C is replaced by continuous liquid-phase oxidation of chromite ore in the KOH SMS media at 300°C in an airlift multiphase reactor, as seen in Fig. 7.

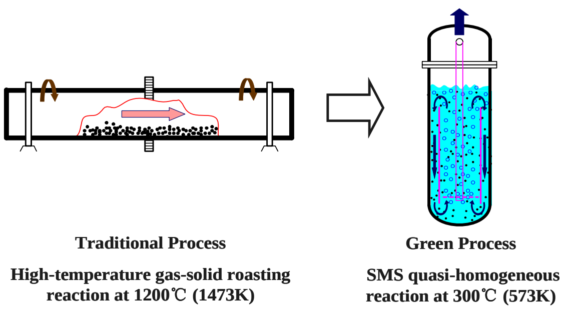


Fig. 7. Reaction Mode Innovation in the Green Process with SMS Media

Technical Indices Comparison

Table 1 showed the technical indices comparison of the green SMS process with the traditional process (Zheng, 2006 and Zhang, 2005). The green process achieved higher extraction yield chromium and zero emission of chromium-containing residue.

Table 1. Technical Indices Comparison of the Green Process with the Traditional Process When Producing 1.0 tonne of $K_2Cr_2O_7$ (in Green Process) or $Na_2Cr_2O_7$ (in Traditional Process)

Item	Green Process	Traditional Process
Chromium recovery yield, %	99	76
Chromium-containing residue, t/t	0.5 (zero emission[1])	2.5
Chromium content in residue, %	0.5	3.0
Hexavalent chromium content in residue, %	0.15	0.7
Chromium-containing waste gas and dust	Almost eliminated	Significant problem
Chromite ore consumption, t	1.07	1.35-1.50
Alkali consumption, t	Below 0.5 (KOH)	0.9 (Na_2CO_3)

Atom Economy Evaluation

Due to the comprehensive utilization of the associated elements such as Al, Mg, and Fe in chromite ore, the atom economy (Trost, 1991) of the green process was much higher than that of the traditional process (Zhang, 2005), as shown in Table 2.

Table 2. Atom Economy Evaluation for the Green Process and the Traditional Process

Item		Green Process	Traditional Process
Atom Utilization	Cr, %	98	76
	Fe, %	95	0
	Mg, %	80	0
	Al, %	90	0
	Na/K, %	98	50
	Ca, %	N/A	0
	S, %	N/A	0
Comprehensive Atom Utilization, %		90.5	14.7

Industrial Scale-up and Demonstration

By use of the green SMS technology described above, a demonstration plant with an annual production capability of 10,000 tonnes of potassium dichromate and 2,000 tonnes of chromic oxide has been built in China (Fig. 8). The technology has exhibited promising results for the industrial production of chromium compounds.

[1] The chromium-containing residue in the green SMS process is used to manufacture desulfurization agent and zero emission is achieved.

(a) (b)

Fig. 8. Photographs of the Chromium Compounds Production Demonstration Plant Constructed in China: (a) Whole Scenery of the Plant; (b) Carbonization Tower.

Construction of Universal Technical Platform with SMS Media

Sketch of the SMS Hydrometallurgical Platform

Extended from the environmentally benign processing of chromite with the SMS media, a universal technical platform for hydrometallurgical processing of mineral resources was constructed and the SMS technology was developed. As shown in Fig. 9, the input material of the universal technical platform is amphoteric metal mineral resources. With the SMS unconventional media, the resource is effectively converted in a green multi-component reaction and separation system. Through an integrated platform for environmentally benign hydrometallurgical process, the objectives of comprehensive utilization of resources and source reduction of pollution can be achieved.

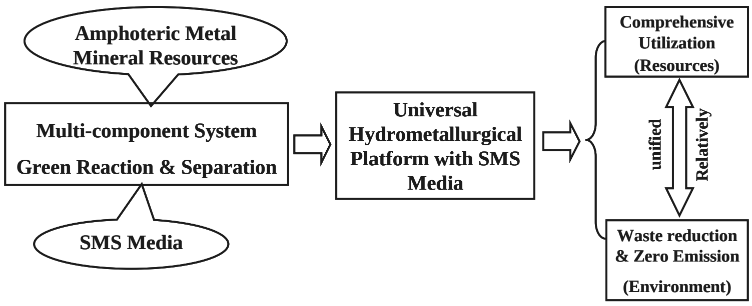


Fig. 9. Sketch of the Universal Hydrometallurgical Platform with SMS Media

Fig. 10 illustrated the target element conversion process for the SMS Platform. The target amphoteric metal oxide minerals are firstly treated with the SMS media and converted into the amphoteric metal oxysalt intermediates, sometimes with the participation of oxygen. The metal oxysalt intermediates are then converted into amphoteric hydroxide hydrate intermediate through hydrolysis or ion exchange process, and sometimes the participation of hydrogen is imperative. By thermal decomposition, the amphoteric hydroxide intermediates can be converted finally into amphoteric oxide products.

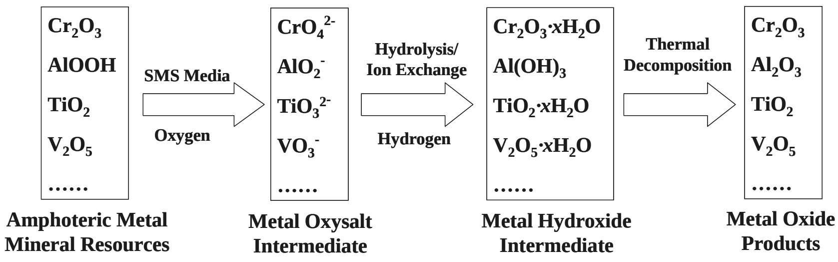


Fig. 10. Target Element Conversion Process for the SMS Platform

Technical Route of the SMS Platform

The SMS platform consists of atom-economic quasi-homogeneous reaction in SMS media, coupling of clean reaction and separation, clean conversion of products, recovery and recycle of media and carriers, and multistage utilization of resource, as can be seen in Fig. 11.

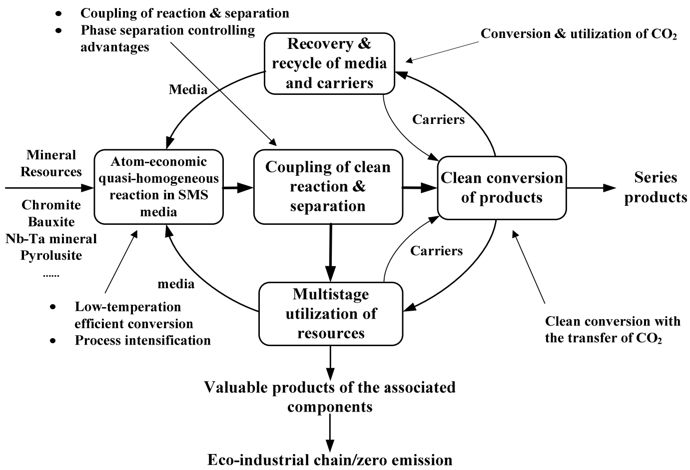


Fig. 11. Technical Route for the SMS Platform (Zhang, 2004)

Applicable Mineral Resources

The universal technical platform with SMS media is generally applicable to varieties of amphoteric metal oxide mineral ore, including Cr, Al, Ti, V, Mn, Nb, Ta, W, Mo, etc. The oxides or hydroxides of these amphoteric metals can react with strong acid as well as strong alkali and produce amphoteric metal oxysalt. The platform has applied to the hydrometallurgical process of chromite, bauxite, and ilmenite. Besides the successful run of the chromium compound demonstration plant, the demonstration plants for manufacturing aluminum oxide and titanium oxide are under construction. The applications of the SMS platform in other amphoteric metals including V, Mn, Nb, Ta have already been investigated in the lab.

Closing Remarks

The SMS unconventional media has excellent physical chemistry properties, which not only simplifies the industrial operation but also helps to intensify the reaction and separation process for the hydrometallurgical processing of mineral resources including Cr, Al, Ti, V, Mn, Nb, Ta, and other amphoteric metals. The universal hydrometallurgical platform with SMS media brings an entirely new approach to environmentally benign hydrometallurgical process. It will effectively resolve the environmental pollution problem in mineral processing industries in such developing countries as China. The application of the SMS platform to the processing of chromite ore has been proven feasible and attractive. The ongoing application of the SMS platform to the processing of other amphoteric metal resources including Al and Ti has exhibited a very promising prospect. The successful development of the SMS environmentally benign technology is revolutionary and will definitely create a new future for hydrometallurgical industries.

Acknowledgements

The authors gratefully acknowledge the financial supports from the National Science and Technology Pillar Program of China (Grant No. 2006BAC02A05), the National Science Foundation of China (Grant No. 50234040), and the National Basic Research Program (973 Program) of China (Grant No. 2007CB613501).

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