

# LABOARTORY SCALE EXTRACTION AND FURTHER TRANSFORMATION OF THE IRON COMPONENT OF RED MUD

Hannian GU<sup>1</sup>, Justin. S. J. HARGREAVES<sup>2</sup>, Jia-Qian JIANG<sup>3</sup> and Jose L. RICO<sup>4</sup>

<sup>1</sup> Key Laboratory of High-temperature and High-pressure Study of the Earth's Interior, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, P. R. China.

<sup>2</sup> WestCHEM, School of Chemistry, Joseph Black Building, University of Glasgow, Glasgow G12 8QQ, UK.

<sup>3</sup> School of Engineering and Built Environment, Glasgow Caledonian University, Glasgow G4 0BA, UK.

<sup>4</sup> Laboratorio de Catálisis, Facultad de Ingeniería Química, Universidad Michoacana de San Nicolás de Hidalgo, Morelia, México.

*guhannian@vip.gyig.ac.cn, justin.hargreaves@glasgow.ac.uk,  
jiaqian.jiang@gcu.ac.uk, jlrico@umich.mx*

## Introduction

Red mud can be divided into Bayer derived red mud and red mud resulting from the sintering alumina process. The sintering alumina process is effectively used for low grade bauxite in China, *i.e.* diasporic bauxite<sup>1</sup>. In addition to this, Bayer derived red mud can mainly be classified into three kinds according to the nature of the bauxite used, *i.e.*, low iron diasporic red mud, high iron diasporic red mud and gibbsitic red mud<sup>2</sup>. For red mud valorisation, it is of importance to take into account chemical and mineral compositions, which are related to its category.

In this study, we have investigated the utilisation of different types of red mud to obtain different higher value end products with an emphasis upon extraction and valorisation of iron content and extraction of valuable trace metals. Gibbsitic red mud, which usually contains high iron content, was applied as a precursor to prepare sodium ferrate (VI) and sodium ferrite following different reaction pathways<sup>3</sup>. Diasporic red mud usually contains higher value trace elements, such as scandium, yttrium, niobium and lithium. Diasporic red mud samples from different sources of origin were investigated in relation to the distribution of trace elements within them.

## Samples and Experiments

Red mud samples from different sources were used in this study, including gibbsite red mud (RM7, SD), high iron diasporic red mud (GX) and lower iron diasporic red mud (HN, GZ1).

RM7, obtained from India, has been described in previous literature<sup>3-5</sup> and has an Fe<sub>2</sub>O<sub>3</sub> content of *ca.* 34-36.8 wt%. Iron-containing solutions were obtained from RM7 using oxalic acid as leaching agent with solid/liquid ratios (grams: milliliters) from 1:10 to 1:30 being applied. In the precipitation process, the solutions were left to stand in natural laboratory light for a couple of days to induce conversion of ferric oxalate into ferrous oxalate ( $\beta$ -FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O) precipitate<sup>3</sup>. Subsequently, this was used as a precursor to prepare sodium ferrate(VI) solution following a wet oxidation method using a ferrous oxalate concentration of 16.67 g L<sup>-1</sup>.<sup>3,6</sup>

Trace elements in three typical red mud samples including GX (from Guangxi province, China), HN (from Henan province, China) and SD (from Shandong province, China) were determined using ICP-OES or ICP-MS. For these samples, the leachability of trace metals using a sequential extraction procedure<sup>7</sup> was compared.

## Results and Discussion

### Synthesis of Ferrate(VI) and Ferrite from Red Mud

It has been reported that as much as 96% of the Fe in red mud can be extracted using 1 mol L<sup>-1</sup> oxalic acid solution as leachant<sup>8</sup>. The ferric oxalate solution can be converted into ferrous oxalate precipitate under conditions of irradiation by UV light or even by just leaving the solution to stand in natural laboratory light for a couple of days. The ferrous oxalate crystallites formed under natural light have greater sizes than those under UV light exposure.

Ferrous oxalate following extraction from red mud and the natural light precipitation process has been used as an intermediate for the preparation of sodium ferrate(VI) as well as sodium ferrite. The ferrate(VI) ion (FeO<sub>4</sub><sup>2-</sup>) possesses strong oxidising potential and generates ferric coagulating species simultaneously when acting as an oxidant for water treatment and environmental remediation. However, the conversion rate of sodium ferrate(VI) solution using Fe<sub>2</sub>O<sub>3</sub> sources as raw materials such as Fe<sub>2</sub>O<sub>3</sub>-NaOH-Na<sub>2</sub>O<sub>2</sub> is less than 50%<sup>3</sup>. The ferrous oxalate was dissolved in HCl solution, then was mixed with the given volumes of the oxidant (sodium hypochlorite, 12% free Cl), and the molar ratios of the oxidant to Fe were 6:1, 8:1, and 10:1, respectively. The concentration of total Fe(II+III) was calculated as 4.5 g/L. After the reaction, the Fe(VI) contents in the ferrate(VI) solutions were 1.7, 2.0, and 2.9 g Fe(VI) L<sup>-1</sup>, corresponding to conversion rates of 38, 44, and 64%, respectively<sup>3</sup>. This has obvious potential benefits in terms of sustainability and also added value for utilisation of red mud waste.

Upon calcination at 500°C, ferrous oxalate was transformed into magnetite (Fe<sub>3</sub>O<sub>4</sub>). Furthermore, the resultant iron oxide, can be applied as a raw material to prepare sodium ferrite by reaction with sodium peroxide.  $\alpha$ -NaFeO<sub>2</sub> or mixtures of  $\alpha$ - and  $\beta$ -NaFeO<sub>2</sub> could be obtained through control of the ratio of magnetite and sodium peroxide at reaction temperatures of 600, 650, and 700°C<sup>3</sup>. Since sodium ferrite might be of interest for energy storage, this provides a route for possible valued-added

utilisation of high iron- containing red mud. Additionally, under 60 mL min<sup>-1</sup> H<sub>2</sub>/Ar for 2 h at 500°C, ferrous oxalate could be transformed into a mixture of iron metal and magnetite, which demonstrates an indirect route to obtain magnetite or iron from red mud, following further optimisation.

### Distribution and Extraction of Valuable Trace Metals from Red Mud

Red mud is considered as a polymetallic raw material and a potential source of both main and trace metals. Extraction of metals from red mud may become economically feasible by using suitable extraction processes<sup>9</sup>. In addition to major components, like iron, aluminium, sodium and titanium, the recovery of valuable trace metals is also of interest. From the elemental analysis (presented in Table 1), diasporic red mud seems to contain higher valuable trace metal content than the gibbsite one. This also depends on the specific bauxite and alumina extraction process, for different diasporic red mud samples significantly vary for one another. For trace valuable metal recovery, it is important to know the occurrence and distribution in red mud samples which should be take account into before extraction or recycling research is undertaken. Tessier's sequential extraction procedure was applied to HN, SD and GX and it was found that 65% of the Li in HN red mud and 60% of the Y in GX could be leached. Other elements, such as La-Lu, Ga, Nb, Sc in these three red mud samples, were leached generally less than 25%. However, the sequential extraction procedure is quite effective to explore the distribution of trace valuable elements, likewise, of trace toxic elements.

**Table 1:** Elemental analysis of diasporic red mud

Elements (µg g <sup>-1</sup> )	Li	Ga	Nb	Ta	Th	U	Hf	Zr	Sc	Y	Σ La-Lu
Accuracy	0.2	0.1	0.2	0.1	0.05	0.05	0.2	2	0.1	0.5	
GX	50.0	49.9	313	23.1	117.5	34.4	77.1	2720	115.5	252	1015.20
HN	224	47.8	108.0	8.5	111.0	33.3	32.3	1090	66.2	83.9	753.64
SD	6.0	59.4	56.4	4.5	56.9	9.11	35.6	1280	54.4	64.1	239.92

### Conclusions

Some different strategies to valorise different red mud samples have been summarised.

Ferrous oxalate extracted from red mud using oxalic acid and precipitated under natural ambient light is an intermediate for the valorisation of red mud to generate ferrate(VI) and ferrite. The conversion rate to sodium ferrate(VI) from ferrous oxalate was as high as 64% when using sodium hydroxide solution with sodium hypochlorite. The Li content in HN was found to be high as 224 µg g<sup>-1</sup>, and ca, 65% was recovered using Tessier's sequential extraction procedure. Around 60% of the Y present in GX could be recovered using the same method. GX, a kind of high iron-containing diaspoire red mud with a CaO content 13.59 wt% was also active for methanol cracking to obtain graphitic carbon and carbon nanofibre composites.

## References

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