RECOVERY OF LITHIUM FROM CHINA CLAY WASTE USING A COMBINATION OF FROTH FLOTATION, MAGNETIC SEPARATION, ROASTING AND LEACHING

Edward Siame MSc, BMinSc

Submitted by Edward Siame to the University of Exeter as a thesis for the degree of Doctor of Philosophy in Earth Resources, February 2011.

I certify that all material in this thesis which is not my own work has been identified and that no material has previously been submitted and approved for the award of degree by this or any other University.

.....(Signature)

ACKNOWLEDGEMENTS

This PhD was made possible by the sponsorship from the Commonwealth Scholarship Commission of the United Kingdom and I am highly grateful.

I sincerely thank my supervisor Dr Richard D. Pascoe for his guidance throughout the research and the writing of this thesis. He was also instrumental in making sure that the material for research and other requisites were readily available.

Thanks to Goonvean Ltd, UK, for allowing us to sample the china clay waste for this research. I would also like to express my gratitude to Mathews Neighbour and Klaas Peter van der Wielen for their assistance with sample collection.

I am also indebted to the Camborne School of Mines technical staff: Ms Sharon Uren, Ms Fiona Thomas and Mr. Steve Pendray for their support during the laboratory and analytical work. Lastly but not the least my regards go to all Camborne School of Mines staff.

ABSTRACT

This study was aimed at recovering lithium from china clay waste using a combination of froth flotation, magnetic separation, roasting and leaching. The china clay waste produced by Goonvean Ltd contains about 0.84% Li_2O and 0.36% Rb_2O, present in some of the mica minerals. Among the mica minerals, zinnwaldite is the major source of lithium with smaller amounts being contributed by muscovite. The results of the flotation tests showed that the dodecylamine collector dosage had a greater effect on the recovery and grade of mica minerals to concentrate than pH over the range tested. It was found that a mica concentrate containing 1.45% Li_2O, 0.55% Rb_2O and 4.47% Fe_2O_3 could be produced at a recovery of 98.6%, 85.2% and 92.8% respectively. Mineralogical analysis of the flotation products showed that the concentrate consisted mainly of muscovite, zinnwaldite and kaolinite with minor amounts of K-feldspar and quartz. The tailing consisted of mainly quartz, K-feldspar and kaolinite with minor amounts of apatite, topaz, zinnwaldite and muscovite.

Further upgrading of the concentrate was found to be possible using a wet high intensity magnetic separator producing a magnetic fraction containing 2.07% Li_2O, 0.74% Rb_2O and 7.42% Fe_2O_3 with a recovery of 73%, 67% and 77% respectively. A mineralogical analysis of the separation products showed that the magnetic fraction consisted of predominantly zinnwaldite with muscovite as the main contaminant. The non-magnetic fraction consisted of muscovite and kaolinite as the main minerals while zinnwaldite, K-feldspar and quartz were subordinate. Electron-microprobe analysis on individual mica grains have shown that zinnwaldite and muscovite contain on average a calculated Li_2O content of 3.88% and 0.13% respectively.

Lithium extraction from the concentrate is only possible after the lithium has been converted into a water-soluble compound. Thus, in order to convert the lithium in concentrate into a water-soluble compound, the gypsum and limestone lithium extraction methods together with the new method of using sodium sulphate were investigated. The process involved roasting a predetermined amount of lithium-mica concentrate with either gypsum, limestone or sodium sulphate at various temperatures and subsequently leaching the pulverised materials in water at 85^oC. A lithium extraction efficiency of about 84% was obtained using gypsum at 1050^oC while rubidium extraction was very low at 14%. It was found possible to extract about 97% Li and 16% Rb if the concentrate was roasted with sodium sulphate at 850^oC. Processing the concentrate with limestone resulted in very low lithium extraction. Iron co-extraction was low in all cases. The XRD analysis of the gypsum and sodium sulphate roast-products showed that the water soluble lithium species were $KLiSO_4$ and $Li_2KNa(SO_4)_2$ respectively.

Preliminary tests on the leach solution obtained by using sodium sulphate as an additive have shown that a Li_2O_3 product with a purity of > 90% could be produced by precipitation with sodium carbonate although more work is required to reach the industrial target of > 99%. The lithium carbonate obtained with Li_2CO_3 content of about 90% is still suitable for use in the glass and ceramic industries, and as feedstock for the production of high-purity lithium compounds. An economic evaluation of the proposed lithium carbonate production plant has indicated an annual rate of return on the investment before tax of 7.2%.

TABLE OF CONTENTS

APPENDICES

LIST OF FIGURES

LIST OF TABLES

Table of Notations

Abbreviation	Full
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence
AAS	Atomic Absorption Spectrometry
LOI	Loss on Ignition
WHIMS	Wet High Intensity Magnetic Separation
μm	microns
wt	weight
g	grams
g/t	gram/tonne
cm^3	Cubic centimetres
H_2SO_4	Sulphuric acid
NaOH	Sodium hydroxide
F	Fluorine
Li	Lithium
wt%	weight percent
MIBC	Methyl Isobutyl Carbinol
S/L/G	Solid/Liquid/Gas
UK	United Kingdom
ppm	Parts per million
DDCL	dodecylamine chloride
w/v%	weight volume percent
Fe	Iron
TGA	Thermal Gravimetric Analysis
DTA	Differential Thermal Analysis
Rb	Rubidium
t	tonnes
USGS	United States Geological Survey
PZC	Point-of-Zero-Charge
SQM	Sociedad Quimica y Minera
$\gamma_{s/a}$	Surface energy between solid and air
$\gamma_{s/w}$	Surface energy between solid and water
$\gamma_{w/a}$	Surface energy between water and air
$W_{s/a}$	Work of adhesion between solid-air interface
θ	Contact angle