Investigations into the Natural Variation of Pyrite Reactivity

Thesis submitted to the School of Chemical and Physical Sciences, Faculty of Science and Engineering, Flinders University in fulfilment of the requirements for the degree of Doctor of Philosophy

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Declaration

"I certify that this thesis does not incorporate without acknowledgment any material previously submitted for a degree or diploma in any university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person except where due reference is made in the text."

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So in the words of the great John Cleese: *“And now for something completely different...”*

Dedicated to my family.

Contents

Publications from this Thesis

1. Osborne, O.D., Pring, A., and Lenehan, C.E., *A simple colorimetric FIA method for the determination of pyrite oxidation rates.* Talanta, **2010**. 82(5), p.1809-1813.

2. Osborne, O.D., Pring, A., Popelka-Filcoff, R.S., Bennett, J.W., Stopic, A., Glascock, M.D., and Lenehan, C.E., *Comparison of the relative comparator and k0 neutron activation analysis techniques for the determination of trace-element concentrations in pyrite.* Mineralogical Magazine, **2012**. 76(5), p.1229-1245.

Summary

Pyrite (FeS_2) is widely accepted to be the most abundant sulfide mineral on the surface of the planet and its abundance in mining waste is well established. The significance of pyrite lies in its potential to oxidise in the environment and cause a process called acid mine drainage. It has been observed that pyrites from different geographical locations will undergo oxidation at different rates, however, the reasons for this are not well understood. This thesis presents investigations into the proposed variation of pyrite reactivity and the mineral characteristics which may contribute to this variation.

A method for the rapid determination of the oxidation rate of naturally occurring pyrite samples was developed. The progress of the oxidation reaction was followed by measurement of the concentration of total dissolved Fe using flow injection analysis. Iron was determined using ultraviolet-visible detection after reaction with the colorimetric reagent 5-sulfosalicylic acid in the presence of ammonia. The calibration function was linear between 5 and 150mg.L^{-1}, and the detection limit was 0.46mg.L^{-1}. The relative standard deviation was typically less than 1% (n=10) and the measurement frequency was 60 per hour. The method was used to quantify the oxidation rate of 40 ground and cleaned pyrite samples (53μm<x<106μm) from various international locations that were subjected to accelerated oxidation in acidic hydrogen peroxide. Results of these experiments showed over a 6-fold difference in oxidation rates across the pyrite samples.

Thirty pyrite samples from a range of geological locations were analysed using relative comparator and k_0-NAA (neutron activation analysis) at MURR (University of Missouri Research Reactor, Columbia, Missouri, USA) and ANSTO (Australian Nuclear Science and Technology Organisation, Lucas Heights, NSW, Australia) respectively. In general, statistical analysis of the trace element data for the two methods showed a good correlation, with the majority of elemental concentrations of paired data reported by MURR and ANSTO being indistinguishable at the 0.05 significance level. Comparison of results presented here for pyrite from Victoria Mine (Spain) compared well with previously published NAA data. Both methods show applicability to the trace element analysis of pyrite.

The trace element data for the samples, collected by NAA was compared to their measured semiconductor types. The results showed that p-type samples generally had an abundance of hole donating impurities while n-type pyrites generally had an abundance of electron donating impurities. Semiconducting type was compared with the reactivity of the samples and no correlation was observed. Interestingly, the inclusion of elements common in clay and silicate layer minerals was found to correlate with sample reactivity. By investigating the geology of samples with large and small measured reactivities a trend emerged indicating that samples from sedimentary origins were significantly more reactive than those from higher temperature hydrothermal origins.

Figures

Tables

Equations

Mechanisms

Abbreviations

%	percent
%RSD	percentage relative standard deviation
%v/v	percent volume for volume
%w/v	percent weight for volume
%w/w	percent weight for weight
°C	degrees Celsius
<	less than
>	greater than
Å	Angstrom
a_0	unit cell dimension
AAS	atomic absorption spectroscopy
AINSE	Australian Institute for Nuclear Science and Engineering
AMD	acid mine drainage
ANSTO	Australian Nuclear Science and Technology Organisation
BET	Brunauer–Emmett–Teller
BSE	backscattered electron
cm	centimetre
$cm^{-2}.s^{-1}$	per centimetre per second
conc.	concentration
CPS	counts per second
DC	direct current
e^-	electron
EDS	energy dispersive X-ray spectrometer
EMF	electromotive force
eV	electron volt
FIA	flow injection analysis
g	gram
h	hour
Hz	hertz
i.d.	internal diameter
i.f	in-line filter
ICP	inductively coupled plasma
ICP-AES	inductively coupled plasma atomic emission spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
$J.cm^{-2}$	joules per centimetre squared
k	rate constant
Kbar	kilobar
km	kilometre
KV	kilovolts
L	litre
LA-ICP-MS	laser ablation inductively coupled plasma mass spectrometry
LTM	Leadville type mineralisation
LOD	limit of detection
LOQ	limit of quantitation

m	metre
M	molar
$M^{-1}.cm^{-1}$	per molar per centimetre
$m^{2}.g^{-1}$	metres squared per gram
Ma	megaannum
mg	milligram
$mg.L^{-1}$	milligrams per litre
min	minute
mJ	millijoule
mL	millilitre
$mL.min^{-1}$	millilitres per minute
mm	millimetre
$mmol.kg^{-1}$	millimole per kilogram
$mol.kg^{-1}$	mole per kilogram
$mol.L^{-1}.min^{-1}$	moles per litre per minute
moles pyrite.$h^{-1}.g^{-1}$	moles of pyrite per hour per gram
MURR	University of Missouri research reactor
mV	millivolt
MΩ	mega ohm
n-type	negative type
nA	nanoamp
NAA	neutron activation analysis
ND	not detected
nm	nanometre
OPAL	open pool Australian lightwater (reactor)
p-type	positive type
PAP	Pouchou and Pichoir
ppb	parts per billion
ppm	parts per million
PT	pressure and temperature
QC	quality control
RM	reference material
s	second
SEM	scanning electron microscope
SRM	standard reference material
UV	ultra violet
Unc.	uncertainty
USGS	United States Geological Survey
UV-VIS	ultra violet-visible
vs.	versus
WDS	wavelength dispersive spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence
µL	microlitre
µm	micrometre
µM	micromolar

$\mu M.h^{-1}.g^{-1}$	micromolar per hour per gram
$\mu M.L^{-1}$	micrograms per litre
$\mu mol.kg^{-1}$	micromole per kilogram
$\mu mol.L^{-1}.min^{-1}$	micromolar per litre per minute
$\Omega^{-1}.cm^{-1}$	per ohm per centimetre

Chemical abbreviations

5-SSA	5-sulfosalicylic acid
CoS_2	colbalt sulfide
$Fe(OH)_3$	ferric hydroxide
$Fe(SSA)_3$	acidic iron-sulfosalicylic acid complex
Fe^{2+}	ferrous iron
Fe^{3+}	ferric iron
FeAsS	arsenopyrite
FeS_2	pyrite / iron disulfide
$FeSO_4$	iron sulfate
$FeSO_4.7H_2O$	melanterite
FeSSA	basic iron-sulfosalicylic acid complex
H^+	proton
H_2O	water
H_2O_2	hydrogen peroxide
HCl	hydrocholric acid
HO_2^-	hydroperoxyl ion
NaCl	sodium chloride
O_2	oxygen
$O2^-$	superoxide anion
OH•	hydroxide radical
OH^-	hydroxide anion
PTFE	polytetrafluoroethylene
PVC	polyvinylchloride
S_2^{2-}	disulfide ion
$S_2O_3^{2-}$	thiosulfate
SO_4^{-2}	sulfate
ZnS	zinc sulfide