IMPACT OF REACTIVE CONDITIONS ON METAL OXIDATION STATE FOR MATERIAL RECOVERY FROM WTE ASH

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Earth Engineering Center
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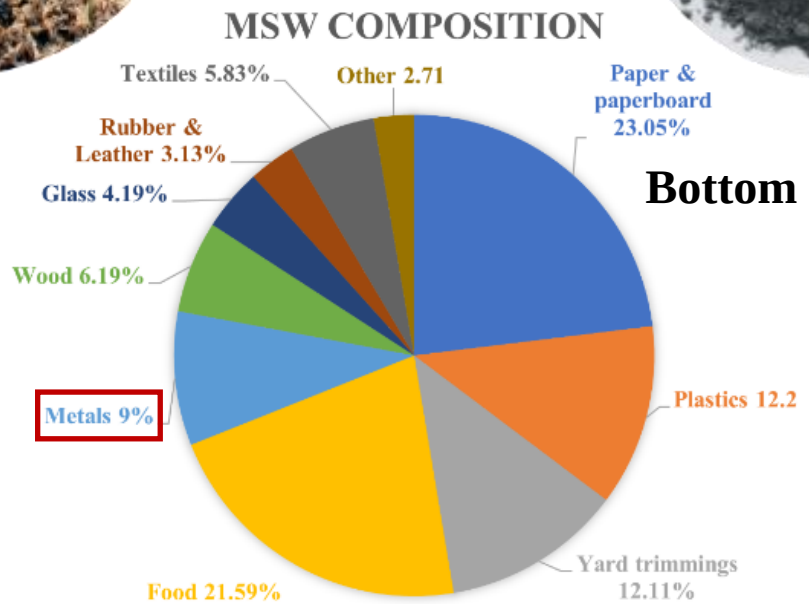
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Critical Material recovery from WTE ash





MSW



Bottom ash (BA)

Focus on recovery of critical materials from MSW may help increase WTE usage

Figure 2.—2023 U.S. Net Import Reliance[1]

Commodity	Net import reliance as a percentage of apparent consumption in 2023	Leading import sources (2019–22)[2]
ARSENIC, all forms	100	China,[3] Morocco, Malaysia, Belgium
ASBESTOS	100	Brazil, Russia
CESIUM	100	Germany
FLUORSPAR	100	Mexico, Vietnam, China, South Africa
GALLIUM	100	Japan, China, Germany, Canada
GRAPHITE (NATURAL)	100	China,[3] Mexico, Canada, Madagascar
INDIUM	100	Republic of Korea, Canada, Belgium
MANGANESE	100	Gabon, South Africa, Australia, Georgia
MICA (NATURAL), sheet	100	China, Brazil, India, Belgium
NIOBIUM (COLUMBIUM)	100	Brazil, Canada
RUBIDIUM	100	China, Germany, Russia
SCANDIUM	100	Japan, China, Germany, Philippines
STRONTIUM	100	Mexico, Germany, China
TANTALUM	100	China,[3] Germany, Australia, Indonesia
YTTRIUM	100	China,[3] Germany, France, Republic of Korea
GEMSTONES	99	India, Israel, Belgium, South Africa
ABRASIVES, fused aluminum oxide	>95	China,[3] Canada, Brazil, Austria
NEPHELINE SYENITE	>95	Canada
RARE EARTHS,[4] compounds and metals	>95	China,[3] Malaysia, Japan, Estonia
TITANIUM, sponge metal	>95	Japan, Kazakhstan, Saudi Arabia, Ukraine
BISMUTH	94	China,[3] Republic of Korea, Belgium, Mexico
POTASH	91	Canada, Russia, Belarus
STONE (DIMENSION)	87	Brazil, China,[3] Italy, Turkey
DIAMOND (INDUSTRIAL), stones	84	India, South Africa, Russia, Congo (Kinshasa)
PLATINUM	83	South Africa, Switzerland, Germany, Belgium
ANTIMONY, metal and oxide	82	China,[3] Belgium, India, Bolivia
ZINC, refined	77	Canada, Mexico, Peru, Republic of Korea
BARITE	>75	India, China,[3] Morocco, Mexico
BAUXITE	>75	Jamaica, Turkey, Guyana, Australia
IRON OXIDE PIGMENTS, natural and synthetic	75	China,[3] Germany, Brazil, Canada
TITANIUM MINERAL CONCENTRATES	75	South Africa, Madagascar, Australia, Canada
CHROMIUM, all forms	74	South Africa, Kazakhstan, Russia, Canada
PEAT	74	Canada
TIN, refined	74	Peru, Bolivia, Indonesia, Malaysia
ABRASIVES, silicon carbide	73	China,[3] Brazil, Canada, Netherlands
SILVER	69	Mexico, Canada, Poland, Switzerland
COBALT	67	Norway, Canada, Finland, Japan
GARNET (INDUSTRIAL)	67	South Africa, Australia, China,[3] India
RHENIUM	60	Chile, Canada, Germany, Kazakhstan
ALUMINA	59	Brazil, Australia, Jamaica, Canada
VANADIUM	58	Canada, Brazil, Austria, Russia
NICKEL	57	Canada, Norway, Finland, Russia
DIAMOND (INDUSTRIAL), bort, grit, and dust and powder	56	China,[3] Republic of Korea, Ireland, Russia
MAGNESIUM COMPOUNDS	52	China,[3] Israel, Canada, Brazil
GERMANIUM	>50	Belgium, China, Canada
IODINE	>50	Chile, Japan
MAGNESIUM METAL	>50	Canada, China,[3] Israel, Taiwan
SELENIUM	>50	Philippines, Mexico, Germany, Canada
TUNGSTEN	>50	China,[3] Germany, Bolivia, Vietnam
SILICON, metal and ferrosilicon	<50	Brazil, Russia, Canada, Norway
COPPER, refined	46	Chile, Canada, Mexico
ALUMINUM	44	Canada, United Arab Emirates, Bahrain, Russia
PALLADIUM	37	Russia, South Africa, Italy, Canada
LEAD, refined	35	Canada, Mexico, Republic of Korea, Australia
MICA (NATURAL), scrap and flake	28	China, Canada, India, Finland
PERLITE	26	Greece, China, Mexico
LITHIUM	>25	Argentina, Chile, China, Russia
TELLURIUM	>25	Canada, Germany, Philippines, Japan
SALT	25	Canada, Chile, Mexico, Egypt
BROMINE	<25	Israel, Jordan, China[3]
ZIRCONIUM, ores and concentrates	<25	South Africa, Australia, Senegal, Russia
CEMENT	22	Turkey, Canada, Greece, Mexico
VERMICULITE	20	South Africa, Brazil, Zimbabwe

100%

~70%

~50%

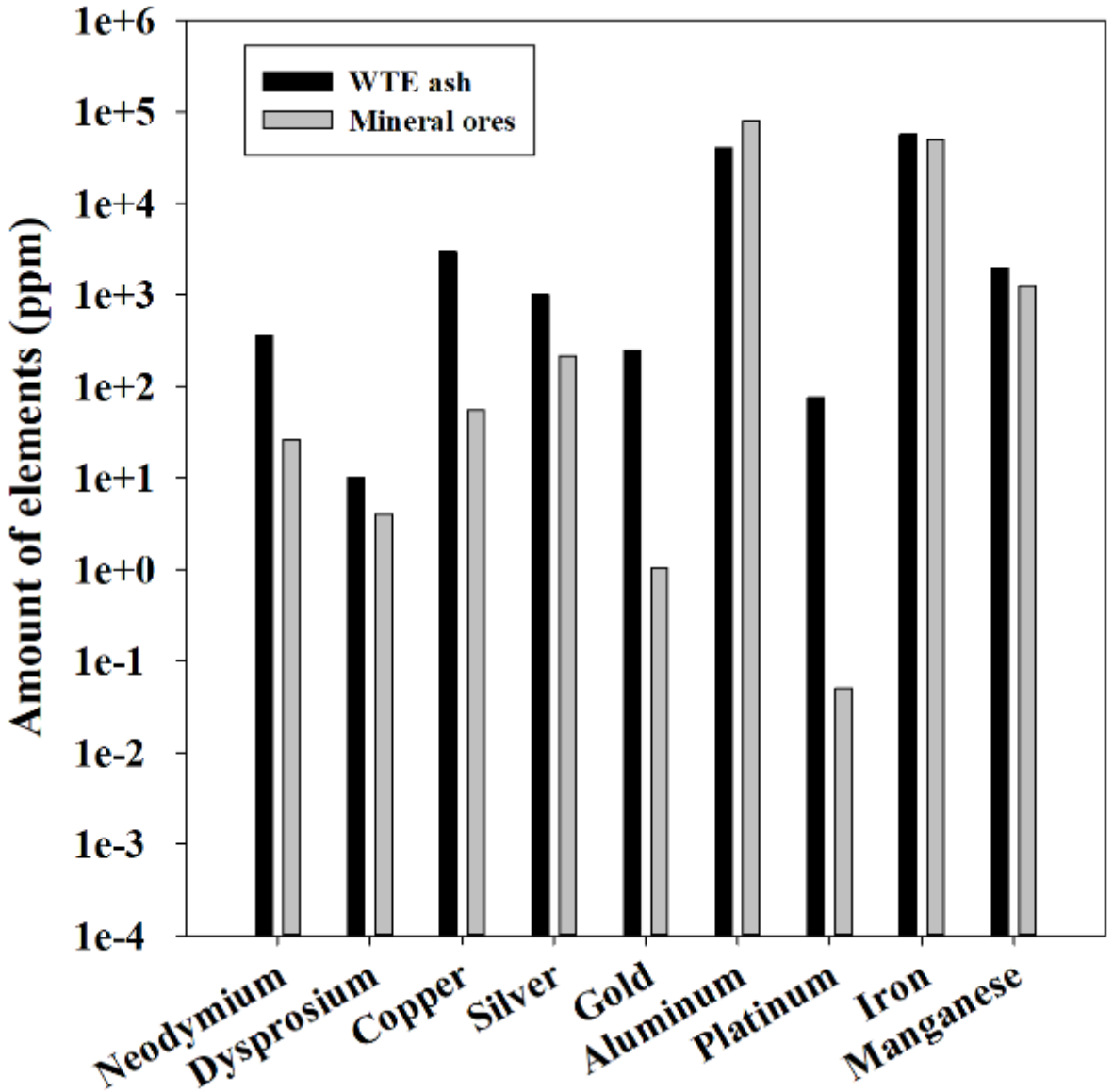
~20%

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U.S. Geological Survey, 2024, Mineral commodity summaries 2024

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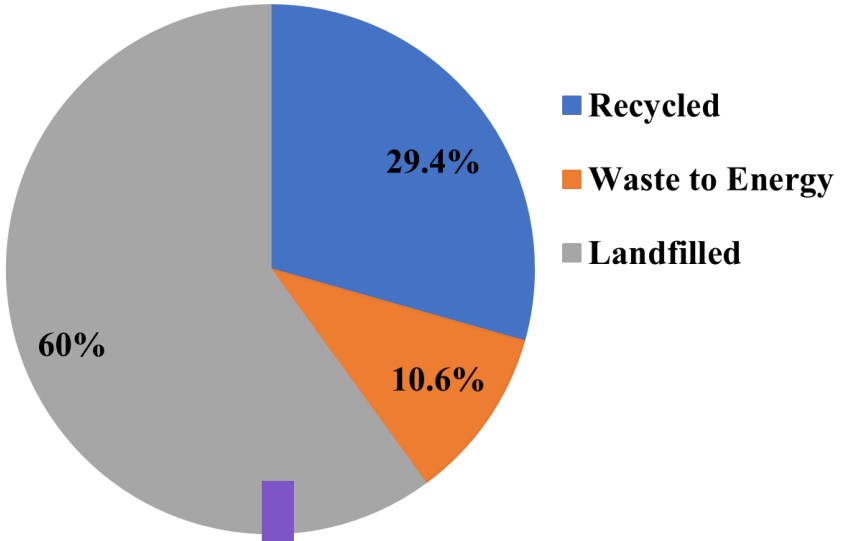
Elements in WTE ash vs mineral ores



Additional elements can be recovered from waste, conserving natural resources

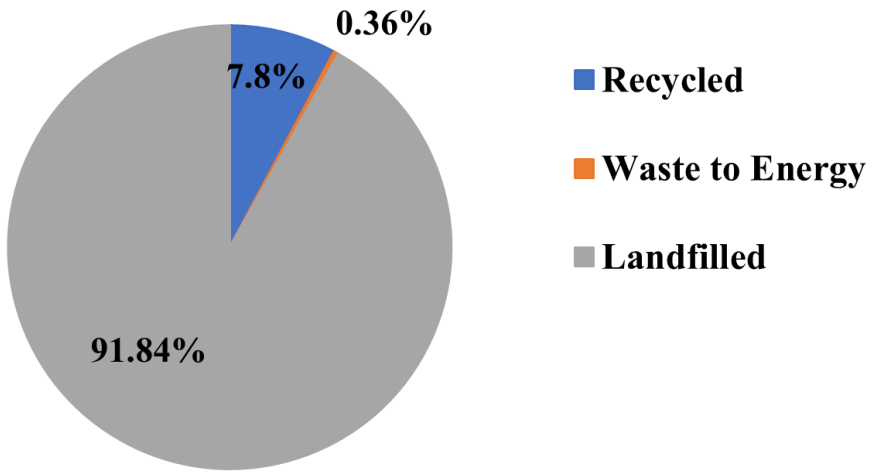
Material recovery - Current scenario

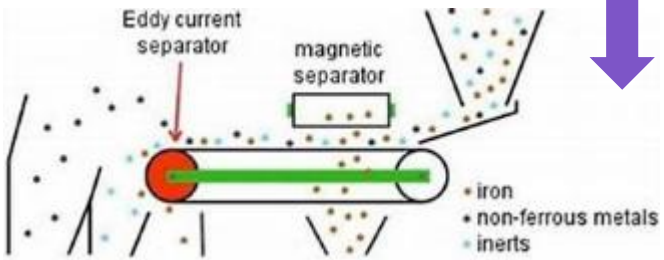
Ferrous metals recovery from MSW

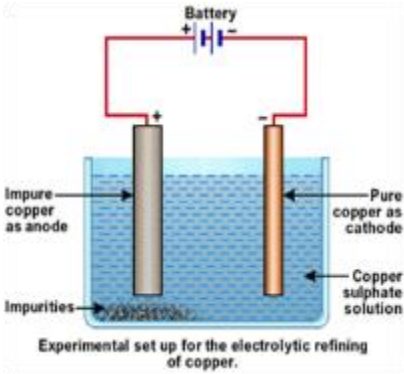




Non-Ferrous metals recovered from MSW









More focus on recovery of non-ferrous metals

US-E.P.A., National Overview_ Facts and Figures on Materials, Wastes and Recycling

Conversion of metal oxidation state



Mn_2O_3 TiO_2 Al_2O_3 Fe_3O_4

WTE Bottom ash

+



Gypsum waste for oxidation adjustment

Different waste stream (additive)

High-temperature (550°C)

Solid-state reactions

Mn_3O_4 $CaTiO_3$ $Ca_2Al_2SiO_7$ Fe_2O_3

Material recovery

Reactions between waste streams → material recovery

Why gypsum as additive?



Gypsum ($CaSO_4.2H_2O$)

- Gypsum is a part of construction and demolition waste
- ~98% landfilled
- Landfilled = H_2S gas generation
- Mineral reduction ($M_xO_y \rightarrow M_aO_b$)

Experimental systems and techniques

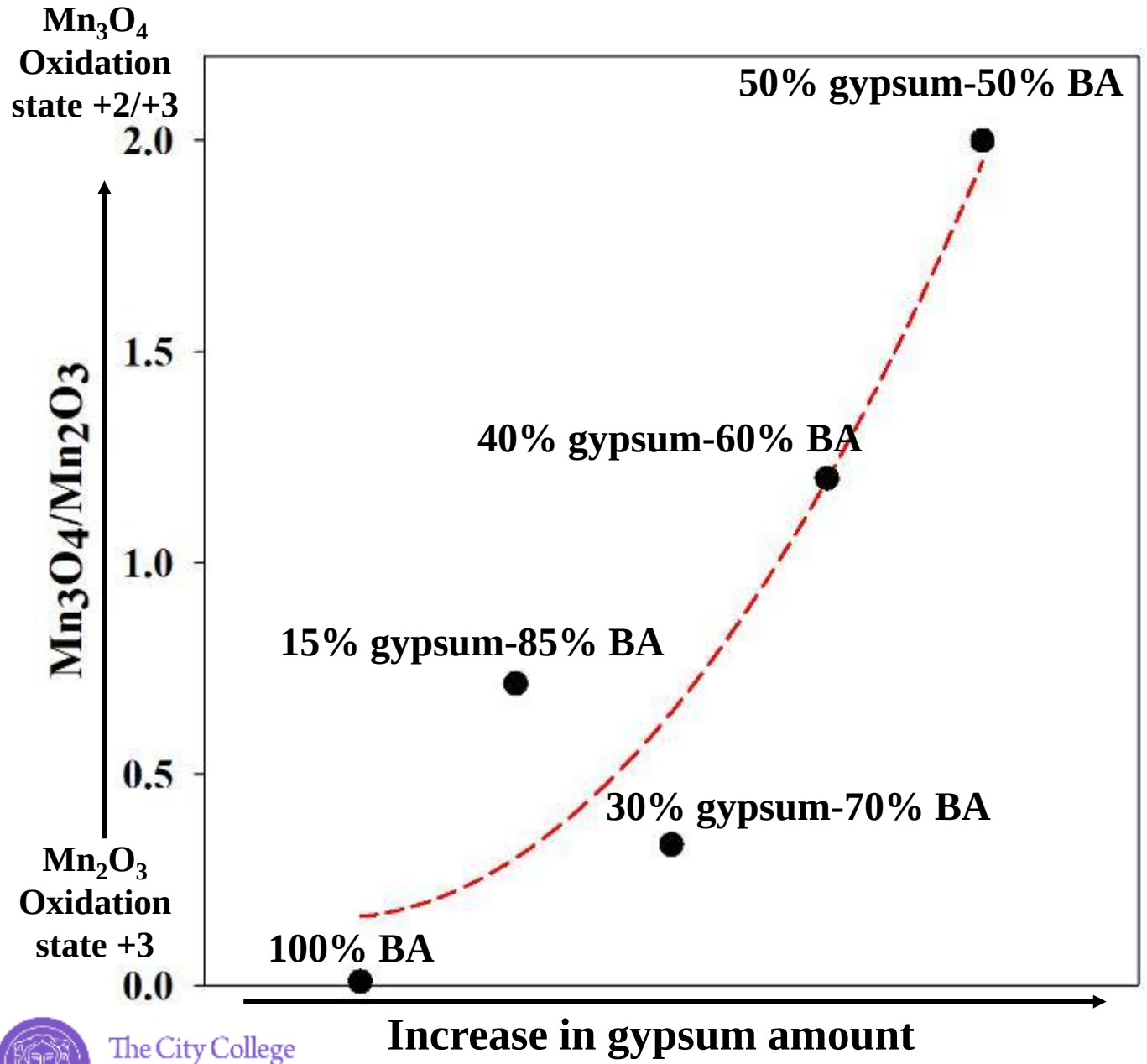
Bottom ash- gypsum samples thermal treatment (**550°C**)



Characterization techniques

XRD	SEM/EDS	TGA	Micro-GC	FT-IR
X-ray diffraction	Scanning Electron Microscopy	Thermogravimetric analyzer	Gas Chromatography	Fourier Transform – Infrared Spectrometry

Change in Mn compounds

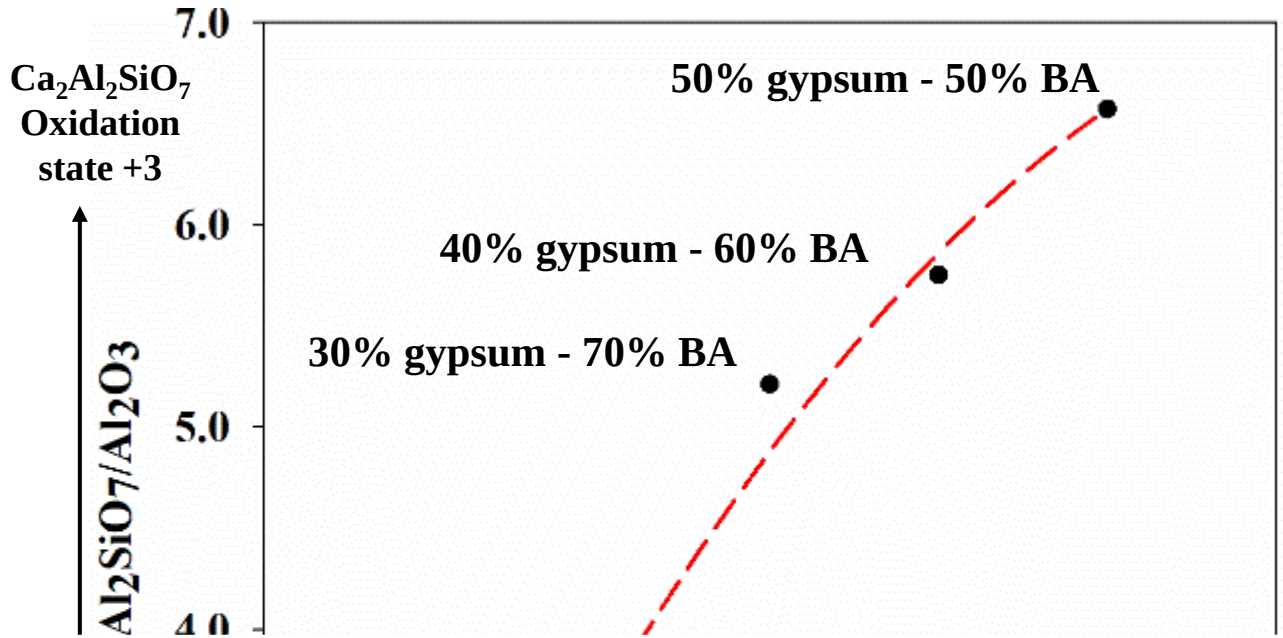


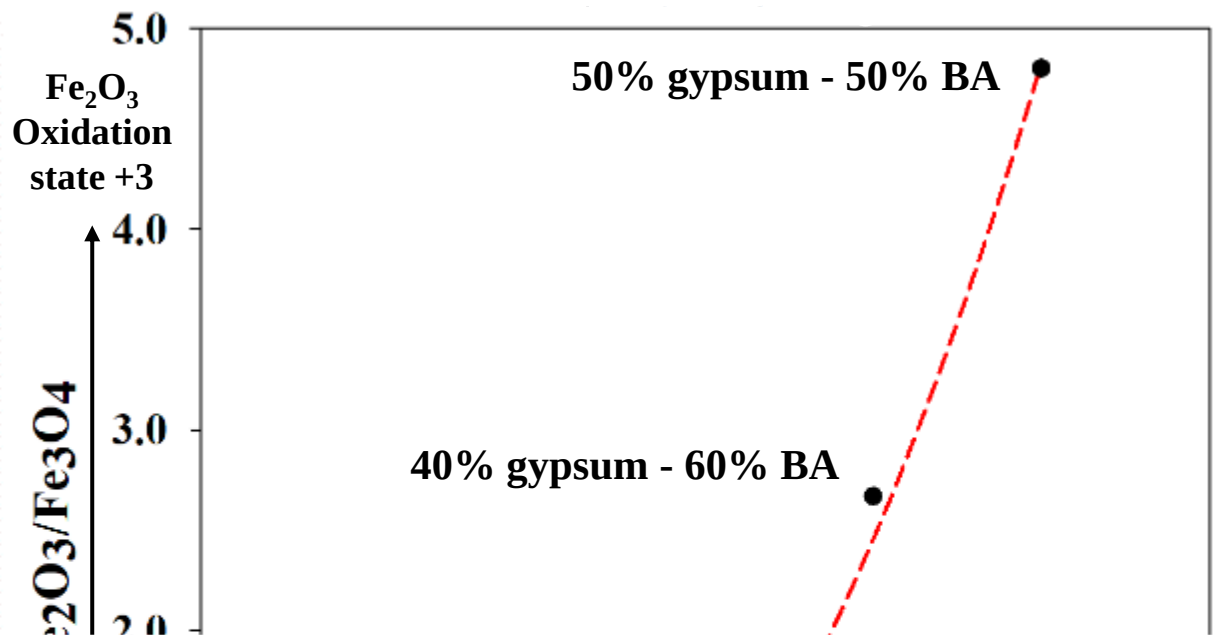
- ↓ Mn_2O_3 ↑ **Mn_3O_4**
- Mn_3O_4 → in **0.05 M** of H_2SO_4, t = 70 min
- Mn_2O_3 → in **2.6 M** of H_2SO_4, t = 140 min
- **~98%** ↓ in concentration of H_2SO_4
- H_2SO_4 energy requirement = 35-50kWh/tonne of H_2SO_4

Gypsum addition →increase Mn recovery

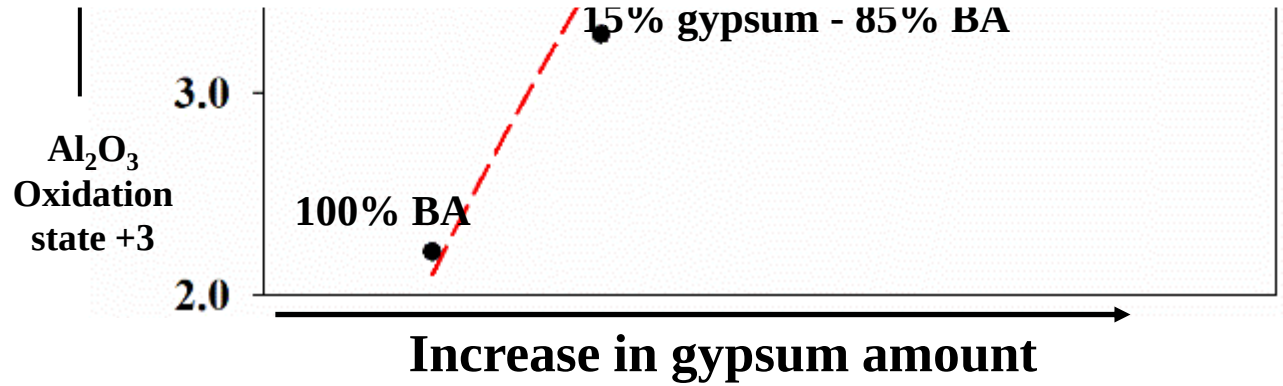
*Artamonova, I.V et al., Engineering, 2013. **05**(09): p. 714-719.*

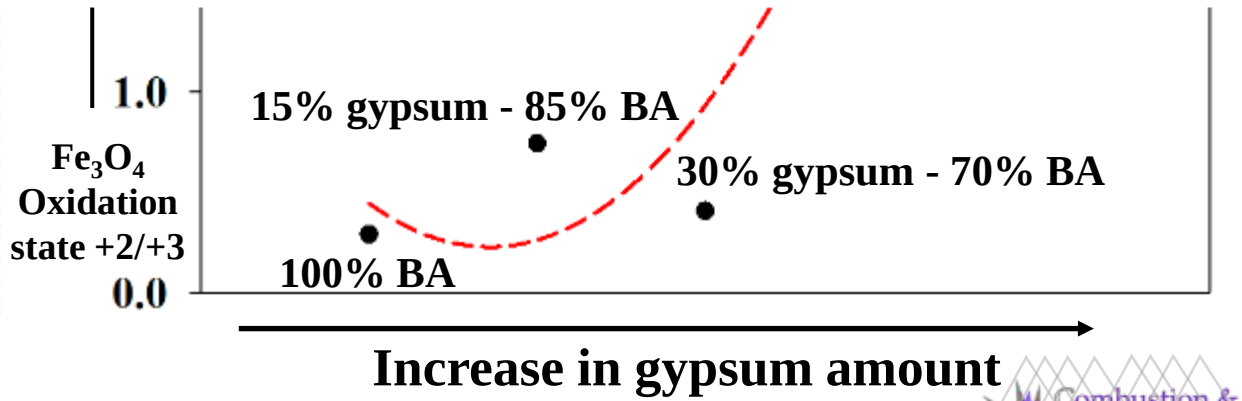
Change in Al and Fe compounds



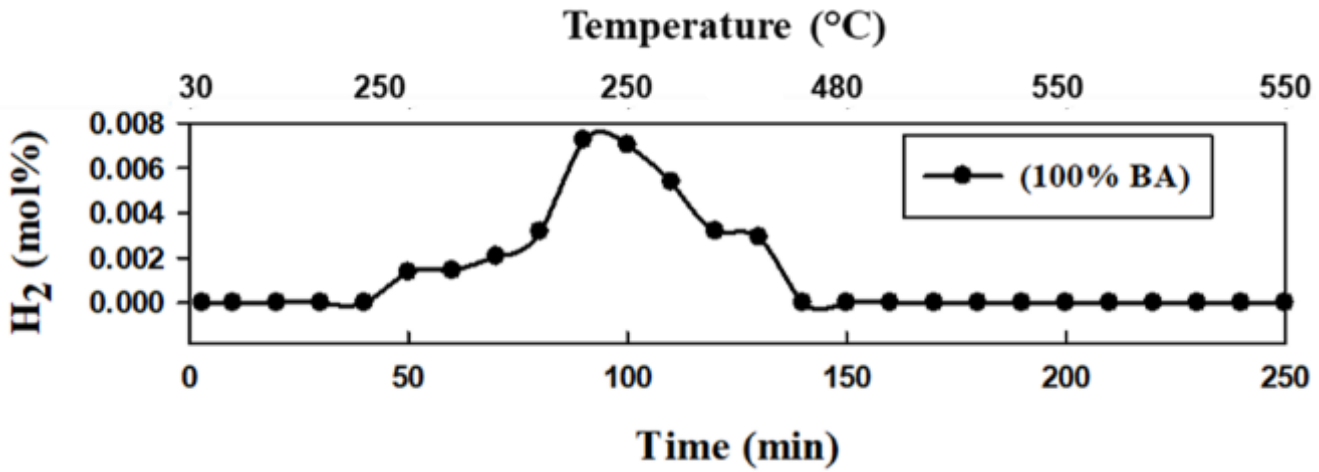


Gypsum addition convert Al and Fe compounds into more extractible phase





Thermal analysis of 100% BA

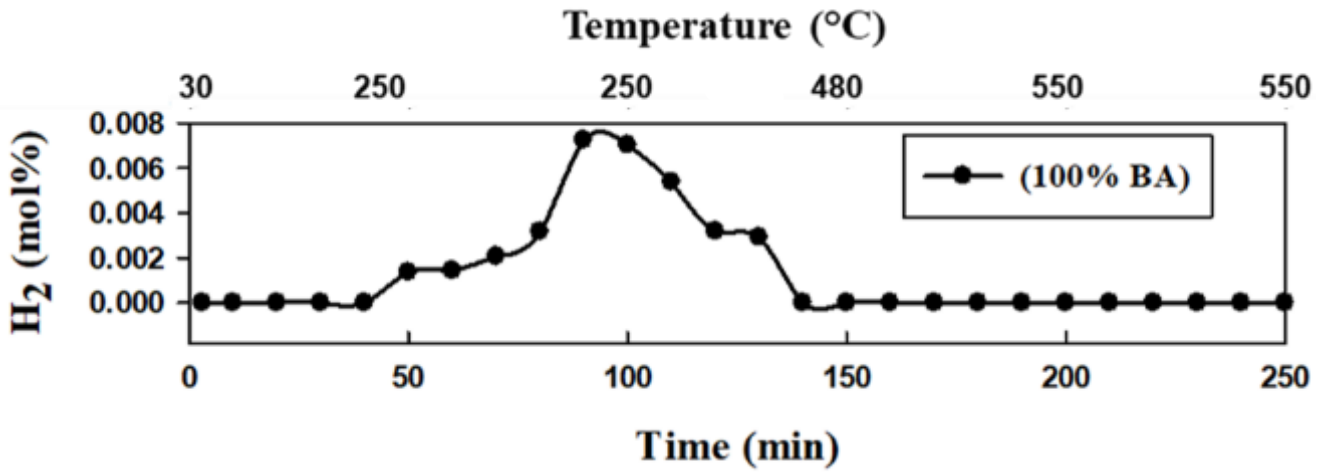


- Evolution of gases
- Dehydration reactions releasing H_2O reacts with metallic Al

Possible reactions:

a. $2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2$
b. $2Al + 4H_2O \rightarrow 2AlO(OH) + 3H_2$
c. $2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2$

Thermal analysis of 100% BA

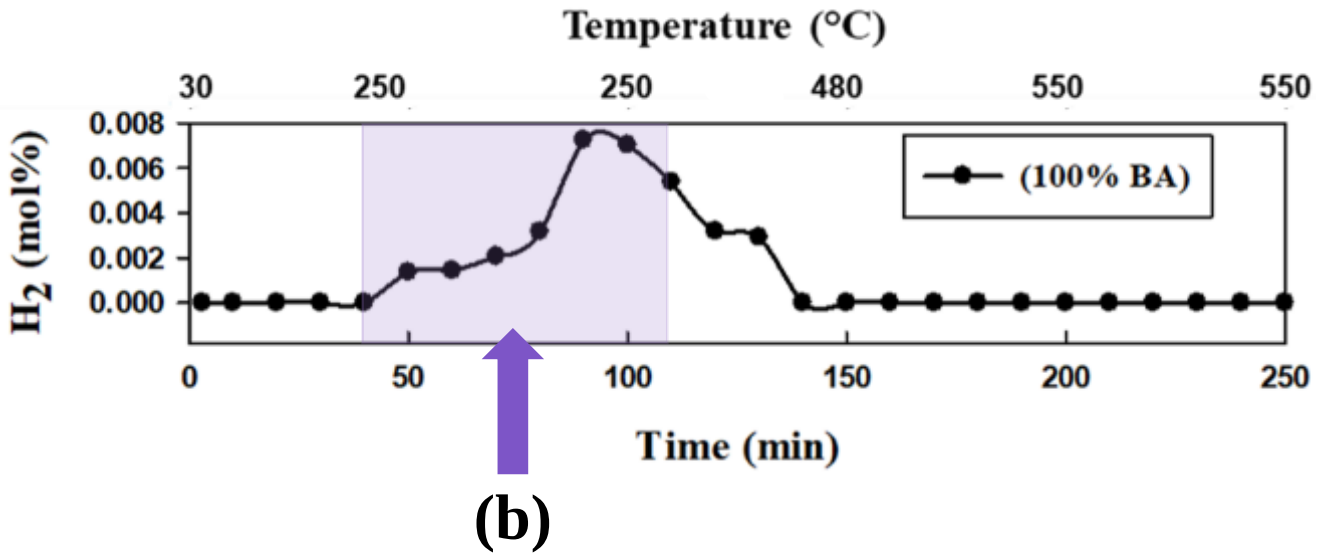


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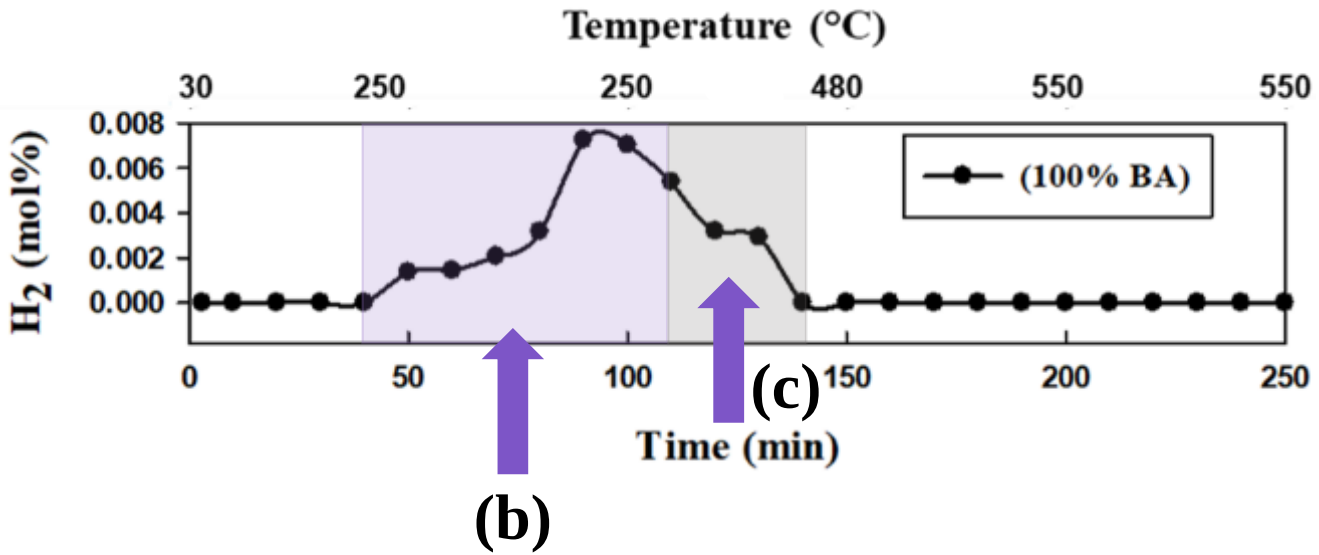
(b)

- Evolution of gases
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Thermal analysis of 100% BA



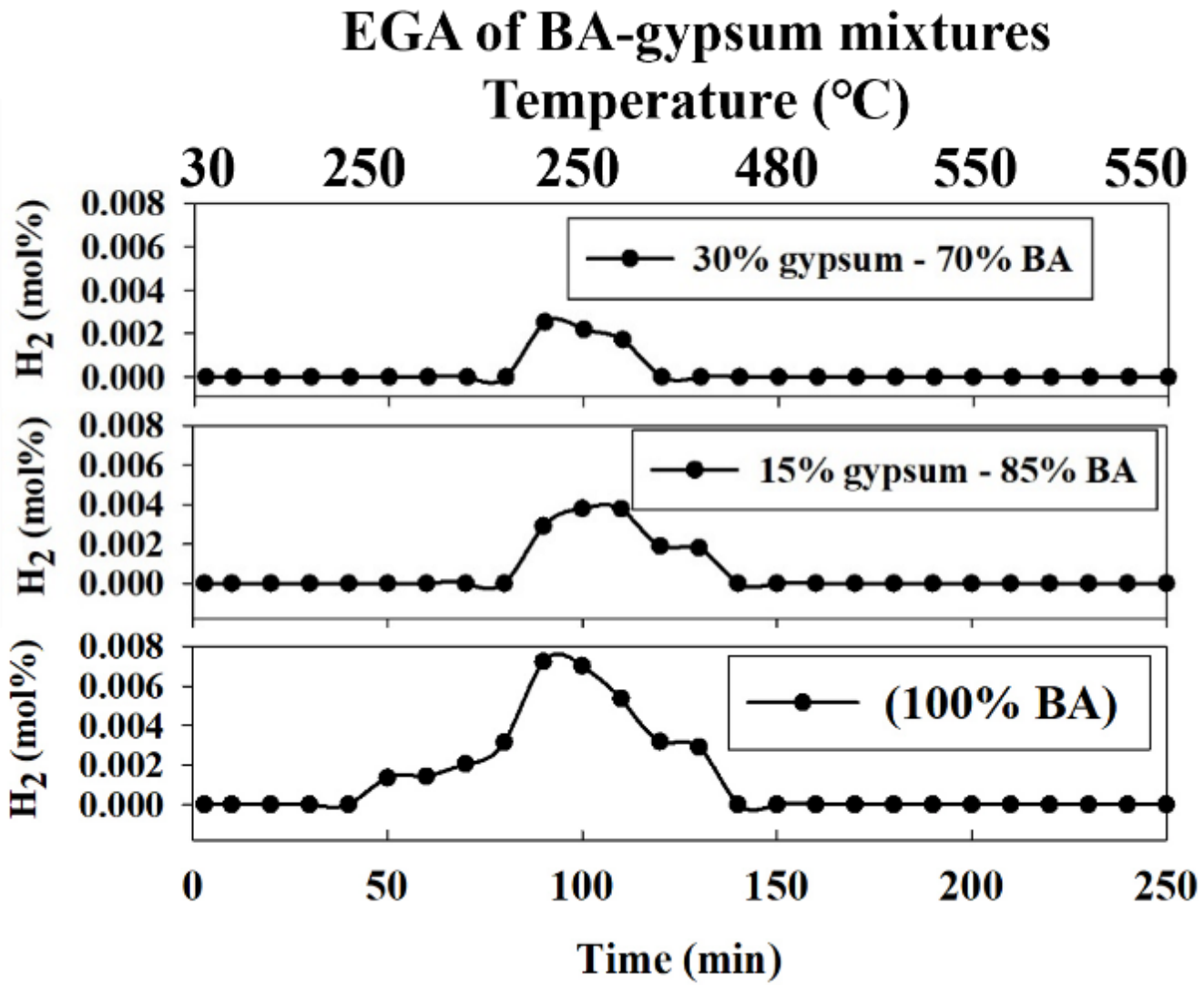
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c. $2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2$

Most favorable reactions → b and c

Thermal analysis of BA-gypsum mixtures



- ↓ Al_2O_3 ↑ **$Ca_2Al_2SiO_7$**
- Conversion of **Al to $Ca_2Al_2SiO_7$** by gypsum addition

Addition of gypsum changes Al compound and decreases H_2 evolution

Summary

- Gypsum addition → changes in metal **oxidation** state (**550℃**)
  - Conversion of **Mn, Fe and Al** into more extractible phase
  - Mn extraction increased by **~20-30%**
  - Increase in gypsum reuse by **30-50%**
  - Phase change in **Al** compounds → reduction in **H_2** gas evolution



Thank you for your attention!

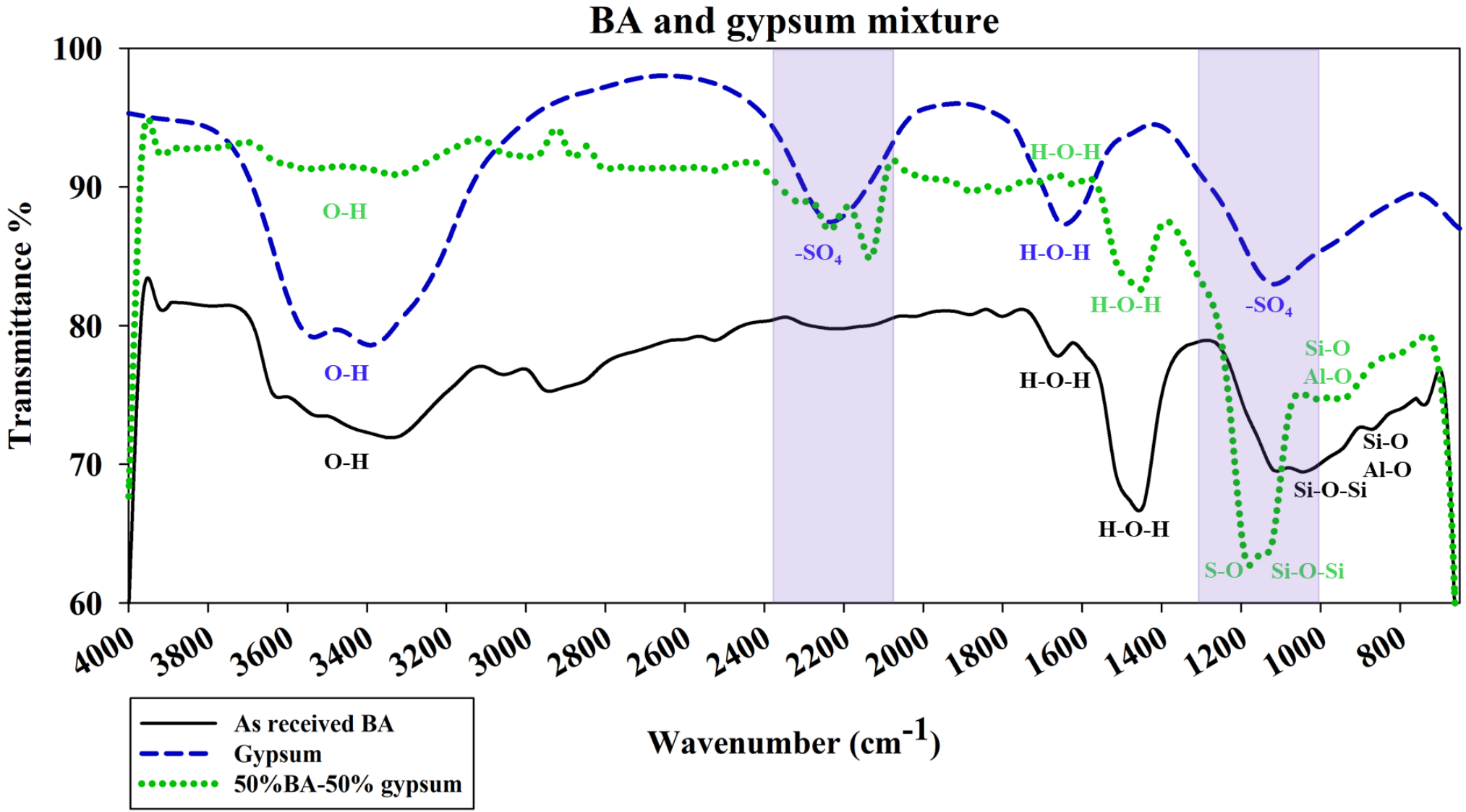
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BA-gypsum reaction confirmed with FTIR results



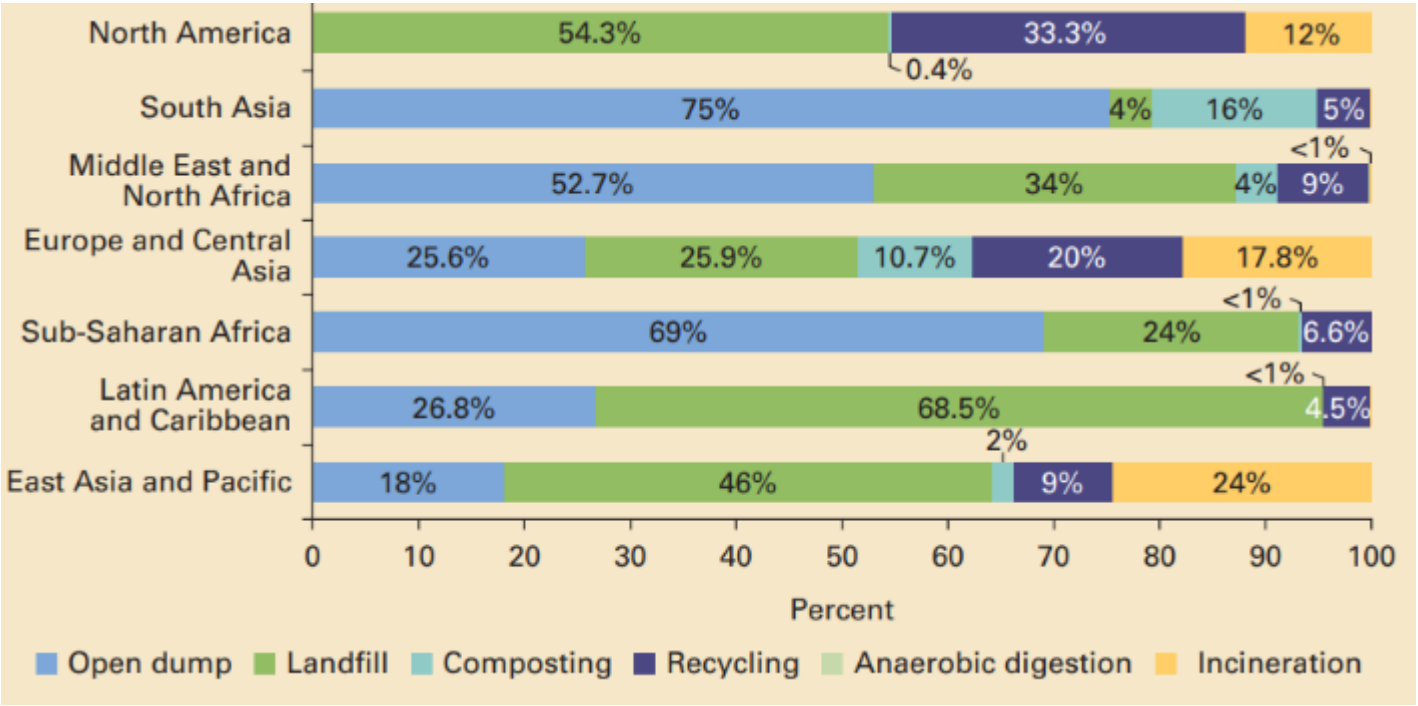
Energy requirements for H2SO4 production

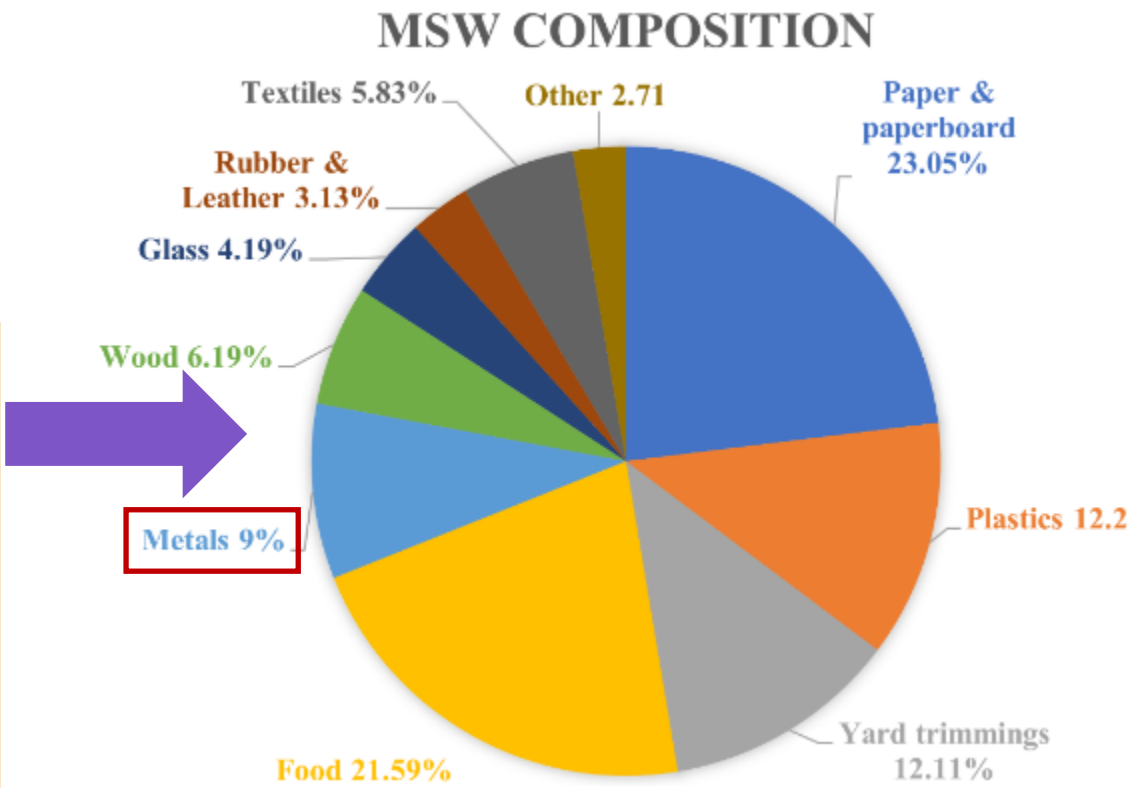
- 18M (~98% conc.) H2SO4= 35-50kWh/tonne of H2SO4
- 2.6 M H2SO4 = ~ 5-8 kWh/tonneof H2SO4
- 0.05 M H2SO4 = ~ 0.1-0.2kWh/tonneof H2SO4

MSW generation

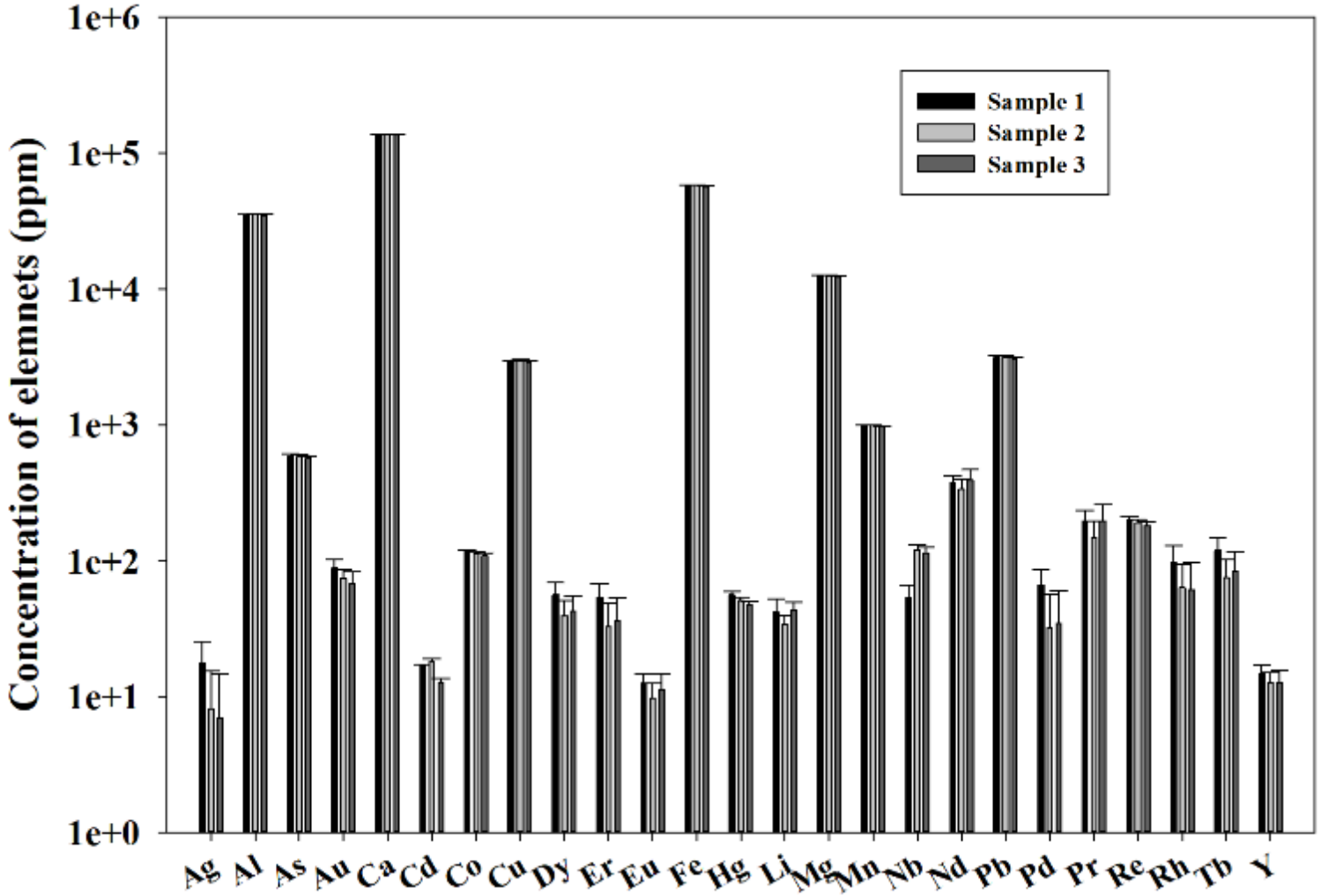
Total MSW generated globally: 2 billion tons in 2019

Estimated to reach 3.4 billion tons by 2050





Focus on recovery of materials from MSW may help engage circular economy

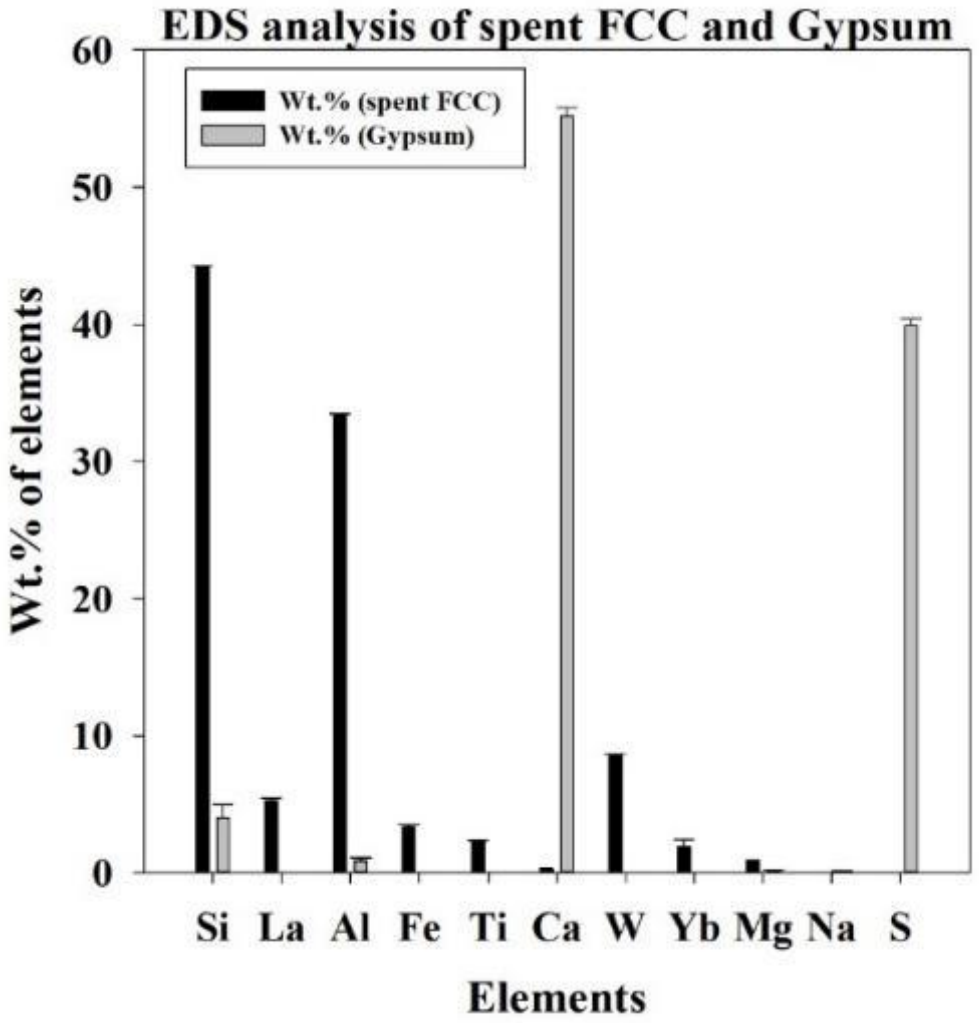

Concentration of elemnets (ppm)
1e+6
1e+5
1e+4
1e+3
1e+2
1e+1
1e+0
Sample 1
Sample 2
Sample 3
Ag Al As Au Ca Cd Co Cu Dy Er Eu Fe Hg Li Mg Mn Nb Nd Pb Pd Pr Re Rh Tb Y

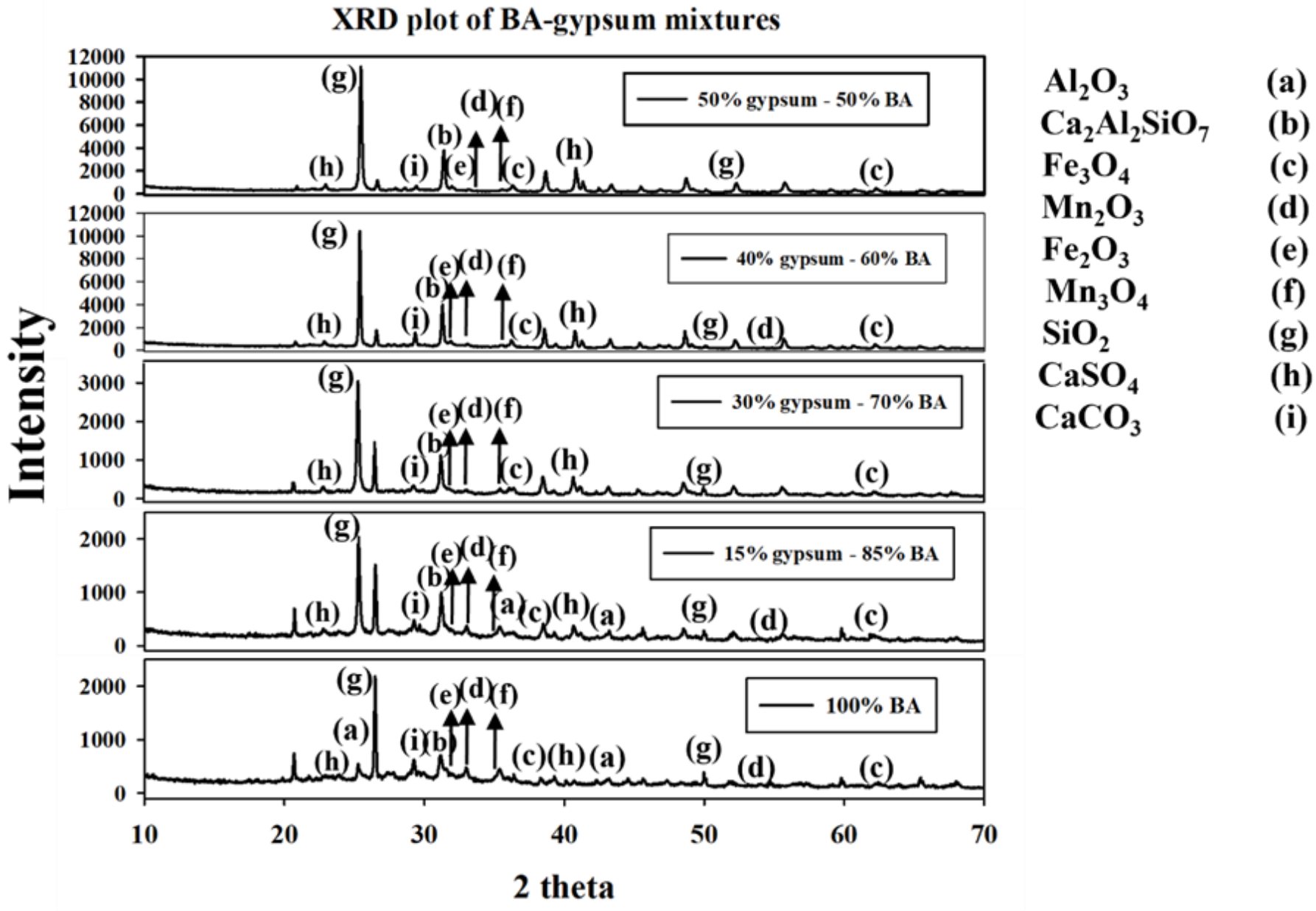
Gypsum wallboard composition

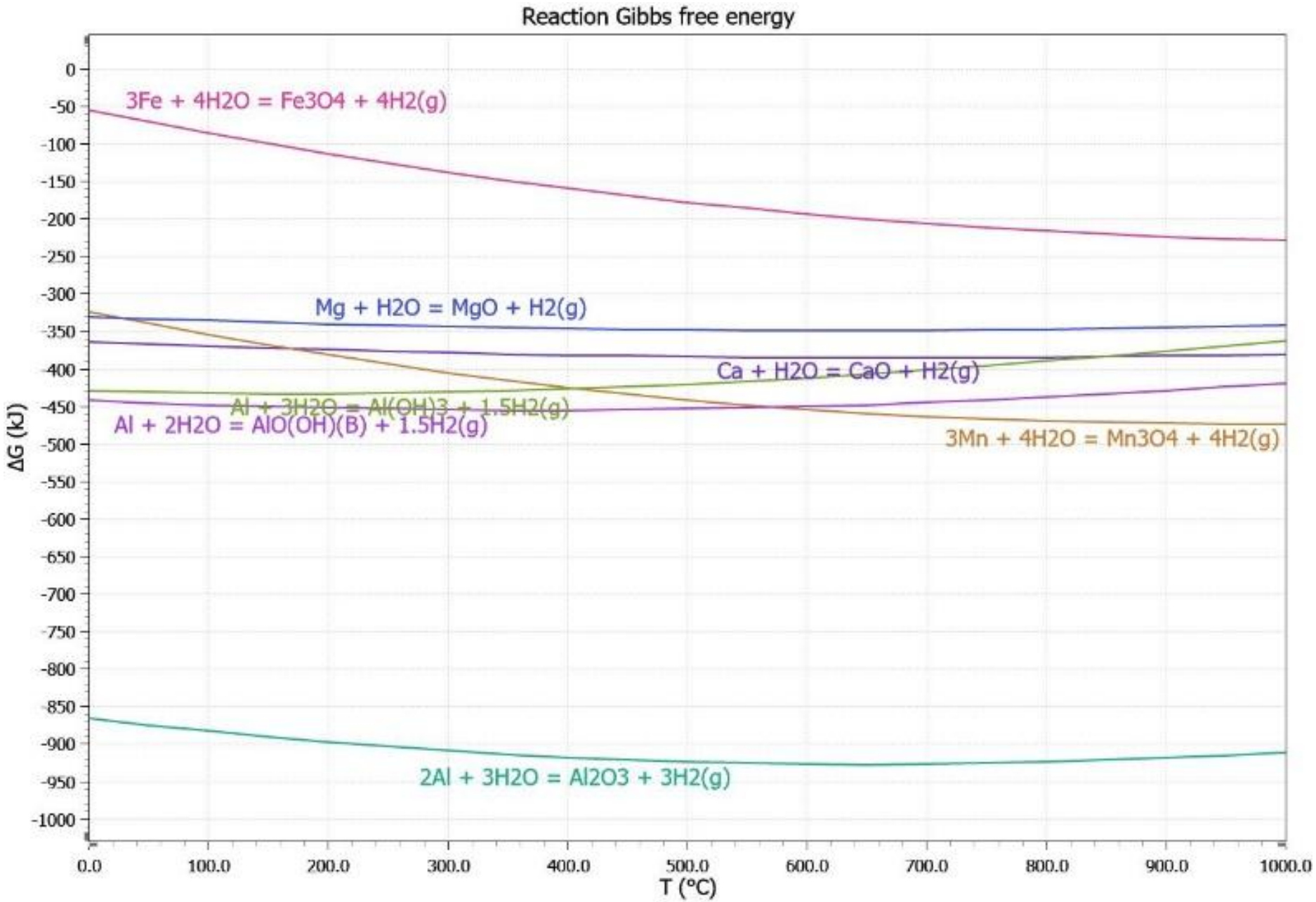
Element	Wt.%
Ca	55.2 ± 0.6
S	39.9 ± 0.5
Si	4 ± 1
Al	0.9 ± 0.2
Mg	0.18 ± 0.05
Na	0.136 ± 0.007

Phases	Formula	Wt.%
Plaster of Paris	$CaSO_4.2H_2O$	96.8
Silica	SiO_2	2.2
Alumina	Al_2O_3	Trace
Magnesium Oxide	MgO	Trace
Calcium Oxide	CaO	Trace

FCC catalyst and gypsum wallboard comparison




XRD plot of BA-gypsum mixtures
Intensity
2 theta
50% gypsum - 50% BA
40% gypsum - 60% BA
30% gypsum - 70% BA
15% gypsum - 85% BA
100% BA
Al2O3 (a)
Ca2Al2SiO7 (b)
Fe3O4 (c)
Mn2O3 (d)
Fe2O3 (e)
Mn3O4 (f)
SiO2 (g)
CaSO4 (h)
CaCO3 (i)


Reaction Gibbs free energy
3Fe + 4H2O = Fe3O4 + 4H2(g)
Mg + H2O = MgO + H2(g)
Ca + H2O = CaO + H2(g)
Al + 3H2O = Al(OH)3 + 1.5H2(g)
Al + 2H2O = AlO(OH)(B) + 1.5H2(g)
3Mn + 4H2O = Mn3O4 + 4H2(g)
2Al + 3H2O = Al2O3 + 3H2(g)
ΔG (kJ)
T (°C)
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
-500
-550
-600
-650
-700
-750
-800
-850
-900
-950
-1000
0.0
100.0
200.0
300.0
400.0
500.0
600.0
700.0
800.0
900.0
1000.0

Possible Mn reactions

Reactions	Energy
$CaSO_4.2H_2O \rightarrow CaSO_4 + 2H_2O$	ΔG = 1.211 kJ/mol
$3\ Mn_2O_3 + CaSO_4 + C \rightarrow 2Mn_3O_4 + CaCO_3 + SO_2$	ΔG = -25.987 kJ/mol
$3Mn_2O_3 + C \rightarrow 2Mn_3O_4 + CO$	ΔG = -56.616 kJ/mol
$6Mn_2O_3 + C \rightarrow 4Mn_3O_4 + CO_2$	ΔG = -233.237 kJ/mol
$3Mn_2O_3 + CO \rightarrow 2Mn_3O_4 + CO_2$	ΔG = -176.62 kJ/mol
$1.5Mn_2O_3 + 2CaSO_4 + 3.25C \rightarrow Mn_3O_4 + 2CaO + 3.25CO_2 + S_2$	ΔG = 274.95 kJ/mol

Step	Temperature Range (℃)	Dwell time (min)	Heating rate (℃/min)
1	30-250	40	5.5
2	250	60	-
3	250-550	30	10
4	550	120	-

Al extraction

Addition of gypsum

- ↓ Al_2O_3 ↑ $Ca_2Al_2SiO_7$
- $Al_2O_3 + CaSO_4.2H_2O + SiO_2 \rightarrow Ca_2Al_2SiO_7 + 2SO_2 + 4H_2O + O_2$

1. $Ca_2Al_2SiO_7 + 10HCl \rightarrow 2AlCl_3 + SiO_2 + 2CaCl_2 + 5H_2O$
2. $Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$

	Reaction 1	**Reaction 2**
Leaching temperature	60℃	100℃
Leaching time	60 min	60 min
Acid concentration	9 M	6 M
Al purity	99.92% (16.09 g/ml)	98.7% (50% recovery)
Other products	SiO2 = 99.8% purity	-

For instance, recycling 10 kg of Al from waste saves 90% energy, equivalent to 13 kg of bauxite residue, 20 kg of CO_2 gas, and 0.11 kg of SO_2 gas.

Al calculations

Samples	Al in Al_2O_3	Al in $Ca_2Al_2SiO_7$	Remaining Al
100% BA	0.4022 gm	0.3307 gm	0.2671 gm
15% gypsum-85% BA	0.213 gm	0.2604 gm	0.3766 gm
30% gypsum-70% BA	0.131 gm	0.2534 gm	0.3156 gm
40% gypsum-60% BA	0.0705 gm	0.1509 gm	0.3786 gm
50% gypsum-50% BA	0.0846 gm	0.0886 gm	0.3268 gm

Samples	Al_2O_3	$Ca_2Al_2SiO_7$
100% BA	0.76 gm	1.68 gm
15% gypsum-85% BA	0.402 gm	1.32 gm
30% gypsum-70% BA	0.247 gm	1.28 gm
40% gypsum-60% BA	0.1334 gm	0.7667 gm
50% gypsum-50% BA	0.16 gm	0.42 gm

Sample	H_2 (mol%)	H2%/ Al
100% BA	0.14	0.14
15% gypsum-95%BA	0.06	0.097
30% gypsum-70%BA	0.028	0.056
50%gypsum-50%BA	0.058	0.194

Samples	Al% in Al_2O_3	Al% in $Ca_2Al_2SiO_7$	Remaining Al%
100% BA	40.22	33.07	26.71
15% gypsum-85% BA	34.35	42	23.65
30% gypsum-70% BA	26.2	50.68	23.12
50% gypsum-50% BA	28.2	28.87	42.267

Fe calculations

Samples	Fe in Fe_2O_3	Fe in Fe_3O_4
100% BA	0.1538 gm	0.5497 gm
15% gypsum-85% BA	0.209 gm	0.2911 gm
30% gypsum-70% BA	0.1 gm	0.2539 gm
40% gypsum-60% BA	0.1865 gm	0.07234 gm
50% gypsum-50% BA	0.3356 gm	0.07234 gm

Samples	Fe_2O_3	Fe_3O_4
100% BA	0.22 gm	0.76 gm
15% gypsum-85% BA	0.299 gm	0.4025 gm
30% gypsum-70% BA	0.143 gm	0.351 gm
40% gypsum-60% BA	0.2667 gm	0.1 gm
50% gypsum-50% BA	0.48 gm	0.1 gm

Mn calculations

Samples	Mn in Mn_2O_3	Mn in Mn_3O_4
100% BA	2.73 gm	0.00216 gm
15% gypsum-85% BA	0.056 gm	0.0414 gm
30% gypsum-70% BA	0.0814 gm	0.028 gm
40% gypsum-60% BA	0.0583 gm	0.07203 gm
50% gypsum-50% BA	0.0139 gm	0.0288 gm

Samples	Mn_2O_3	Mn_3O_4
100% BA	3.93 gm	0.03 gm
15% gypsum-85% BA	0.0805 gm	0.0575 gm
30% gypsum-70% BA	0.117 gm	0.039 gm
40% gypsum-60% BA	0.0838 gm	0.1 gm
50% gypsum-50% BA	0.02 gm	0.04 gm