

# **THE FERRIC ION - GOD'S GIFT TO HYDROMETALLURGISTS TO KEEP 'EM HUMBLE**

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WHEN YOU NEED TO BE SURE



∅ **The first SEx war**

∅ **There's nothing basic about basic iron sulphate**

## History

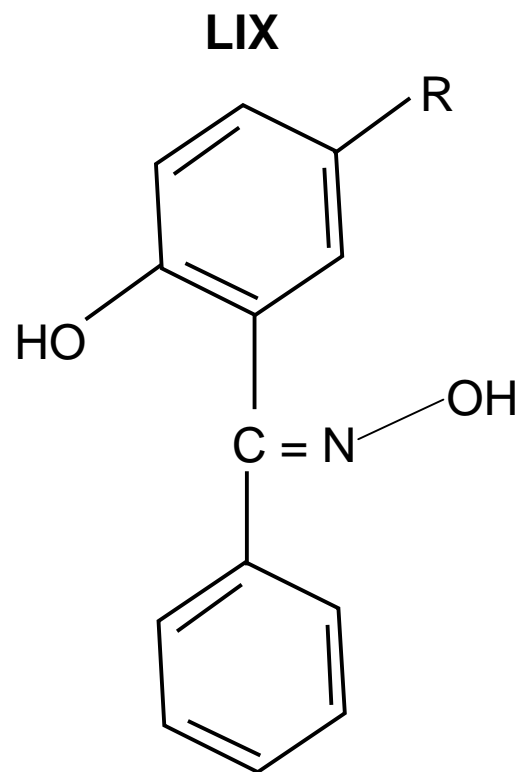
- § Great interest in solvent extraction in the 1960's, initially for uranium and then for copper.
- § Low grade oxide copper ores were being processed in the USA and Chile by acidic heap leaching (small scale).
- § Copper sulphate in solution was recovered by cementation onto scrap iron, and then smelted and refined.
- § Most leach liquors contained ferric ions, which reacted with the scrap iron wastefully, and the process was:
  - (i) Expensive
  - (ii) Yielded an impure copper product

# THE FIRST SEX WAR

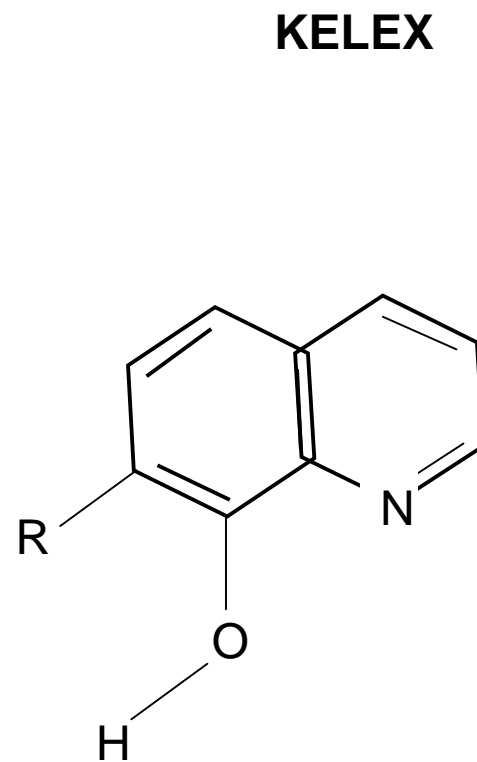
## History

- § Early economic projections predicted the cost of SEx/EW would be half the cost of cementation/smelting/refining.
- § The “perfect” reagent had to be able to extract copper (II) from weak acid leach solution (pH 1-2), be strippable in strong acid (50 -100g/L H<sub>2</sub>SO<sub>4</sub>) to be compatible with EW, and be very selective for copper – particularly versus the ferric ion.
- § Copper SEx reagent development was spearheaded by two US companies, General Mills, who produced the LIX reagents, and Ashland Chemical, who produced Kelex 100.

# COPPER SEX REAGENTS



**HYDROXYOXIME**



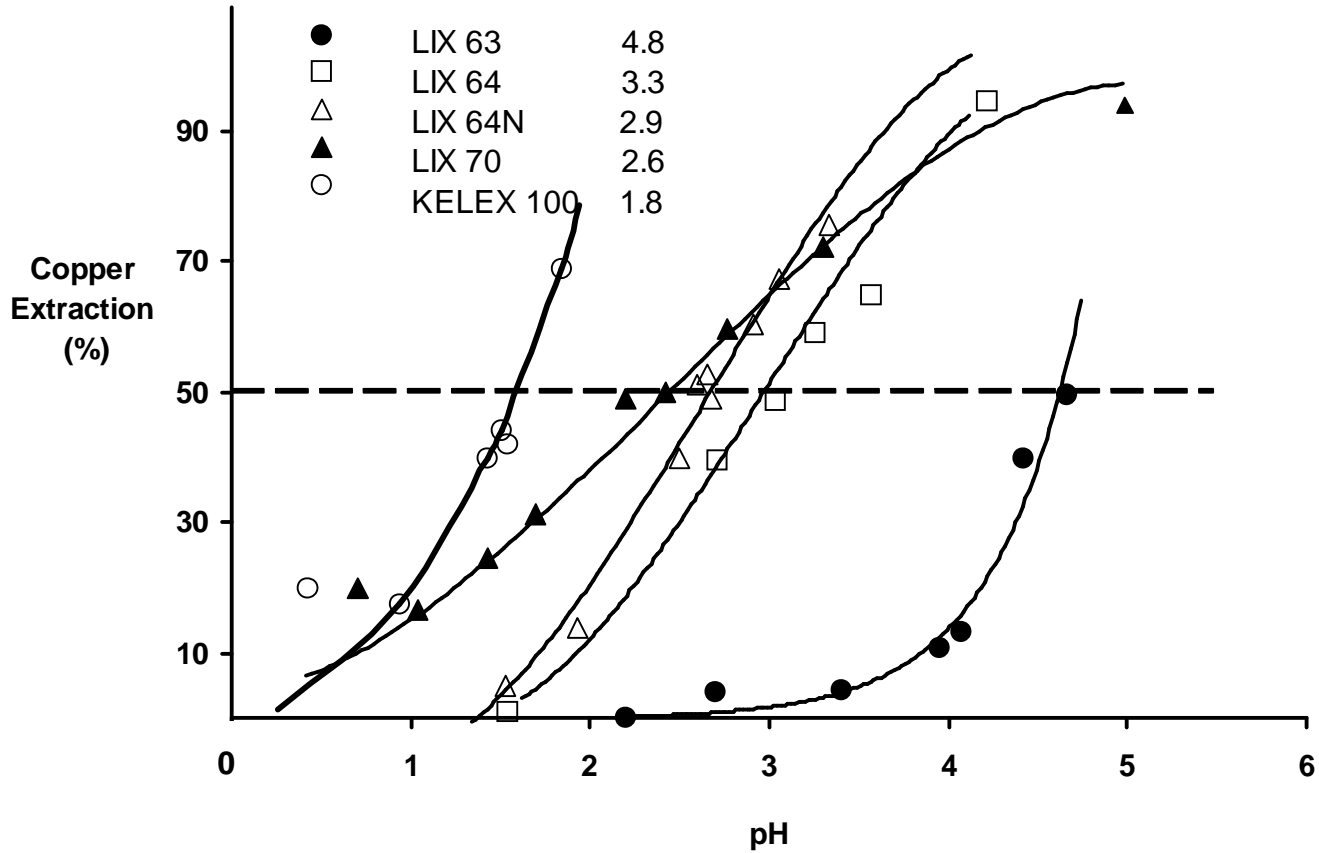
**HYDROXYQUINOLINE**

# THE FIRST SEX WAR

## History

- § The first copper SEx plant was built at the Blue Bird Mine in Arizona in 1968 (6000 tpa Cu), soon followed by a much bigger plant at Nchanga mine in Zambia (65,000 tpa Cu).
- § More plants followed, and 3% of world copper production was via SEx/EW by 1975. By 2007, this had grown to 22% of annual Cu production, (3.5M tons of cathode copper). This was being produced in 70 SEx/EW plants in 16 countries (60% in Chile).
- § But who was making the SEx reagents and who was winning the reagent war?

# Copper extraction with LIX and KELEX reagents as a function of pH



## Initial Rate of Copper Extraction (g/L/min)

**KELEX 100 0.98**

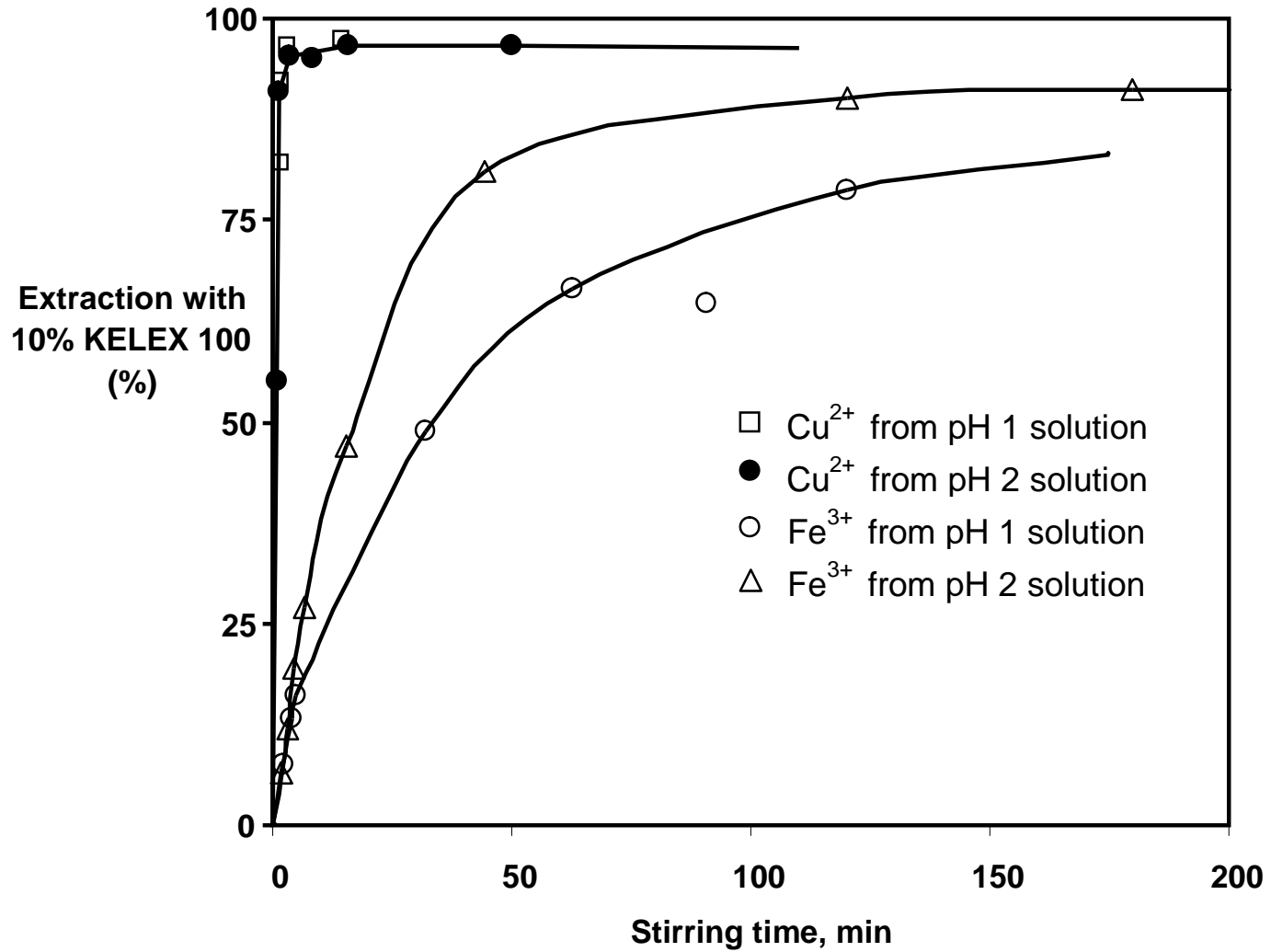
**LIX 64N 0.11**

# KINETIC AND STABILITY CONSTANTS FOR THE REACTION OF Cu(II) AND Fe(III) WITH HYDROXYQUINOLINES

<b>Metal</b>	<b>Initial Rate of Extraction with Kelex 100 (g/L/min)</b>	<b>Stability with 8 Hydroxy Quinoline</b>
Cu(II)	0.98	$\text{Log } \beta_2 = 23.0$
Fe(III)	0.067	$\text{Log } \beta_3 = 36.9$



# RATES OF EXTRACTION OF Cu(II) AND Fe(III) BY KELEX 100



## RATES OF EXTRACTION OF Cu(II) AND Fe(III) BY LIX65N AND ITS PRECUSOR, SALICYLALDOXIME

LIX 65N	Salicyl- aldoxime	Metal Extracted (%)					
		1 h		24 h		432 h	
mol %	mol %	Cu	Fe	Cu	Fe	Cu	Fe
100	0	20	2	38	2	40	2
60	40	39	1	48	1	49	1
20	80	50	2	52	2	55	0.3
0	100	59	1	57	2	61	0.1

## THE MORAL OF THE STORY

If you want to win a SEx war, it is better to be slow and selective than to be fast and flirtatious.

**THERE'S NOTHING BASIC ABOUT  
BASIC IRON SULPHATE**

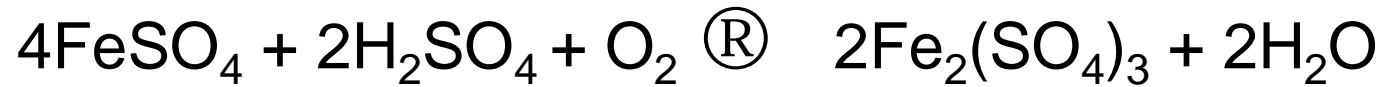
WHEN YOU NEED TO BE SURE



## BACKGROUND

- § Basic iron sulphate (BFS) is a solid compound that is formed under certain conditions during the oxidation of pyrite or other iron sulphide minerals with oxygen at high temperatures in an autoclave.
- § Iron sulphide minerals are oxidized in an autoclave to produce ferric sulphate and sulphuric acid in solution. The ferric sulphate then hydrolyzes slowly, precipitating back out of solution as hematite and/or BFS.

## OXIDATION



Overall:

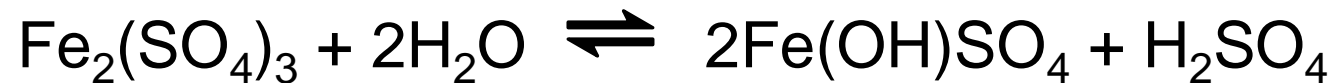


# HYDROLYSIS

Ferric sulphate hydrolyzes to hematite at higher temperatures and lower acidity



and it hydrolyzes to BFS at lower temperatures and higher acidity

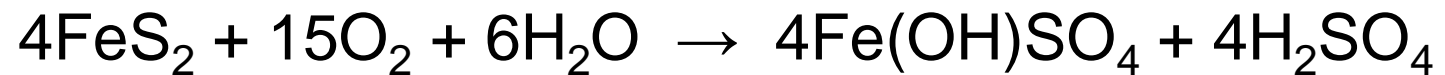


# OXIDATION AND HYDROLYSIS

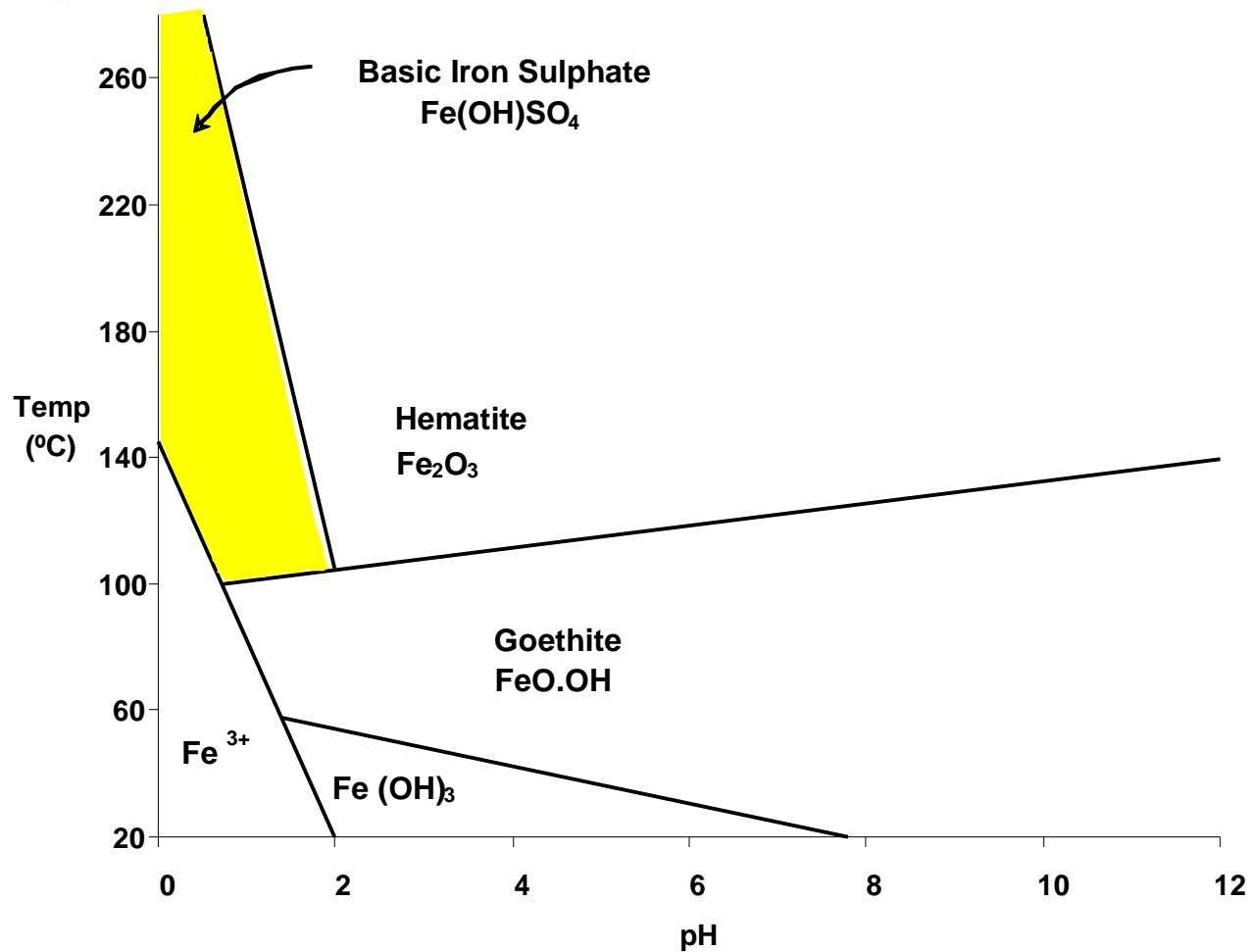
Overall reaction for the oxidation of pyrite to ferric sulphate followed by hydrolysis to hematite



Overall reaction for the oxidation of pyrite to ferric sulphate followed by hydrolysis to BFS



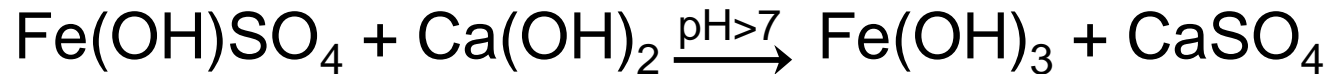




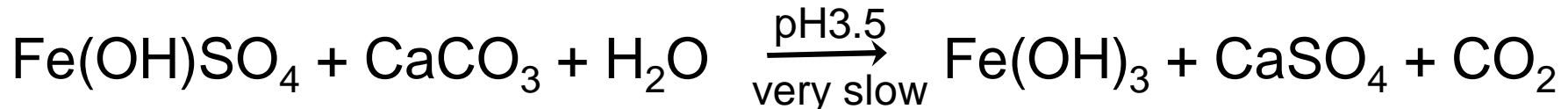
Stability domains of compounds of the ferric ion in water as a function of temperature and pH

# WHY IS BFS BAD NEWS IN A CYANIDATION CIRCUIT?

- § BFS is not basic, it is actually acidic.....and it must be neutralized before cyanidation



- § The rate of release of acid by BFS is extremely slow in weakly acidic solution (pH <7). This means BFS cannot be neutralized with a cheap alkali such as limestone.



## WHY IS BFS BAD NEWS IN A CYANIDATION CIRCUIT?

- § Even under alkaline conditions, the rate of release of acid by BFS is quite slow – but it is persistent at the pH needed for cyanide leaching (pH ~10)
- § Consequently, the pH constantly drifts downwards under normal cyanide leach operating conditions, into the pH region where cyanide is converted to HCN gas.

# WHY IS BASIC IRON SULPHATE BAD NEWS IN CYANIDATION CIRCUITS

- ∅ For health and safety reasons related to HCN formation, the BSF must be fully neutralized prior to cyanidation. This will take 12-24 hours and add significantly to plant capital cost.
- ∅ As a result, most of the sulphate generated in the autoclave has to be neutralized with hydrated lime, rather than limestone. Lime can be at least 10 times the price of limestone.
- ∅ If not dealt with appropriately, the increased capex and opex associated with BFS formation could eliminate POX from consideration for many refractory gold projects



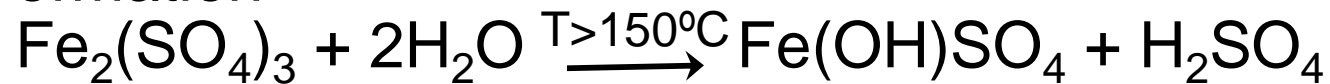
**WHAT IS THE BEST SOLUTION?**

**THE “HOT CURE” PROCESS**

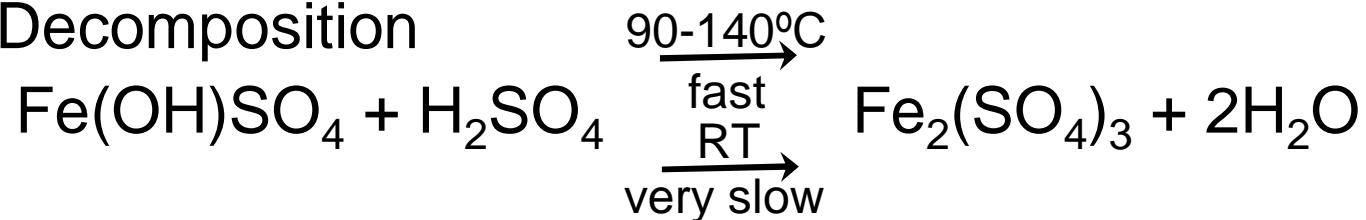
# THE HOT CURE PROCESS

The basis of the hot cure process is the fact that the hydrolysis reaction that produces BFS in the autoclave is reversible at lower temperatures:

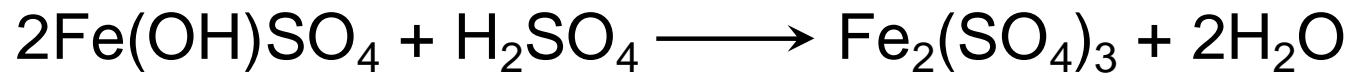
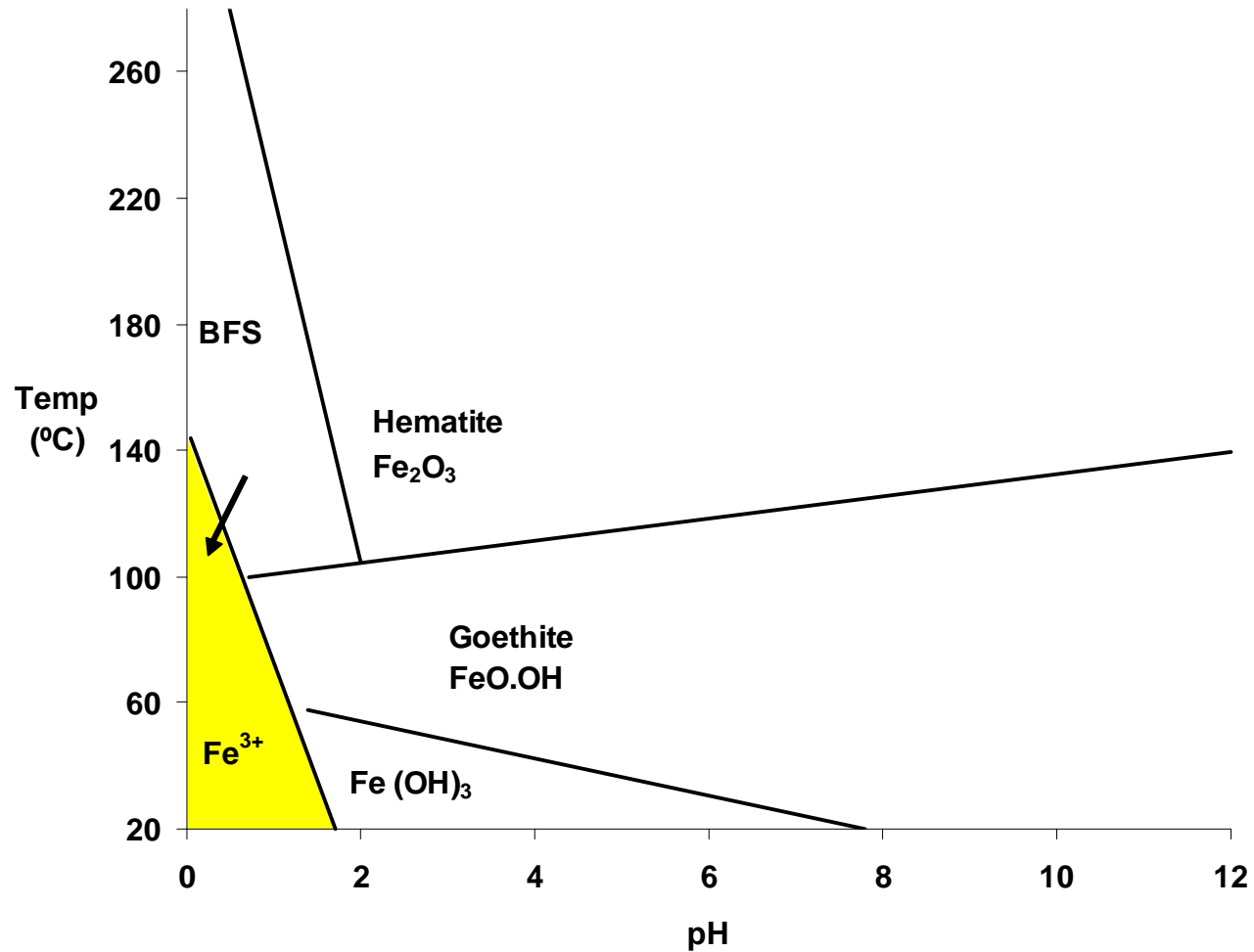
BFS Formation



BFS Decomposition



# THE HOT CURE PROCESS



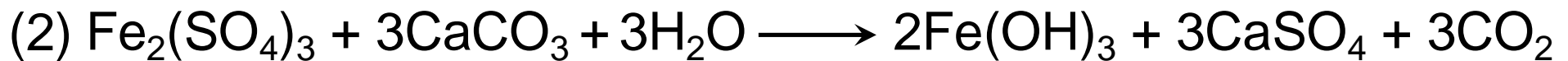
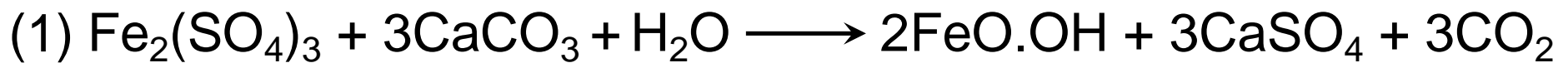
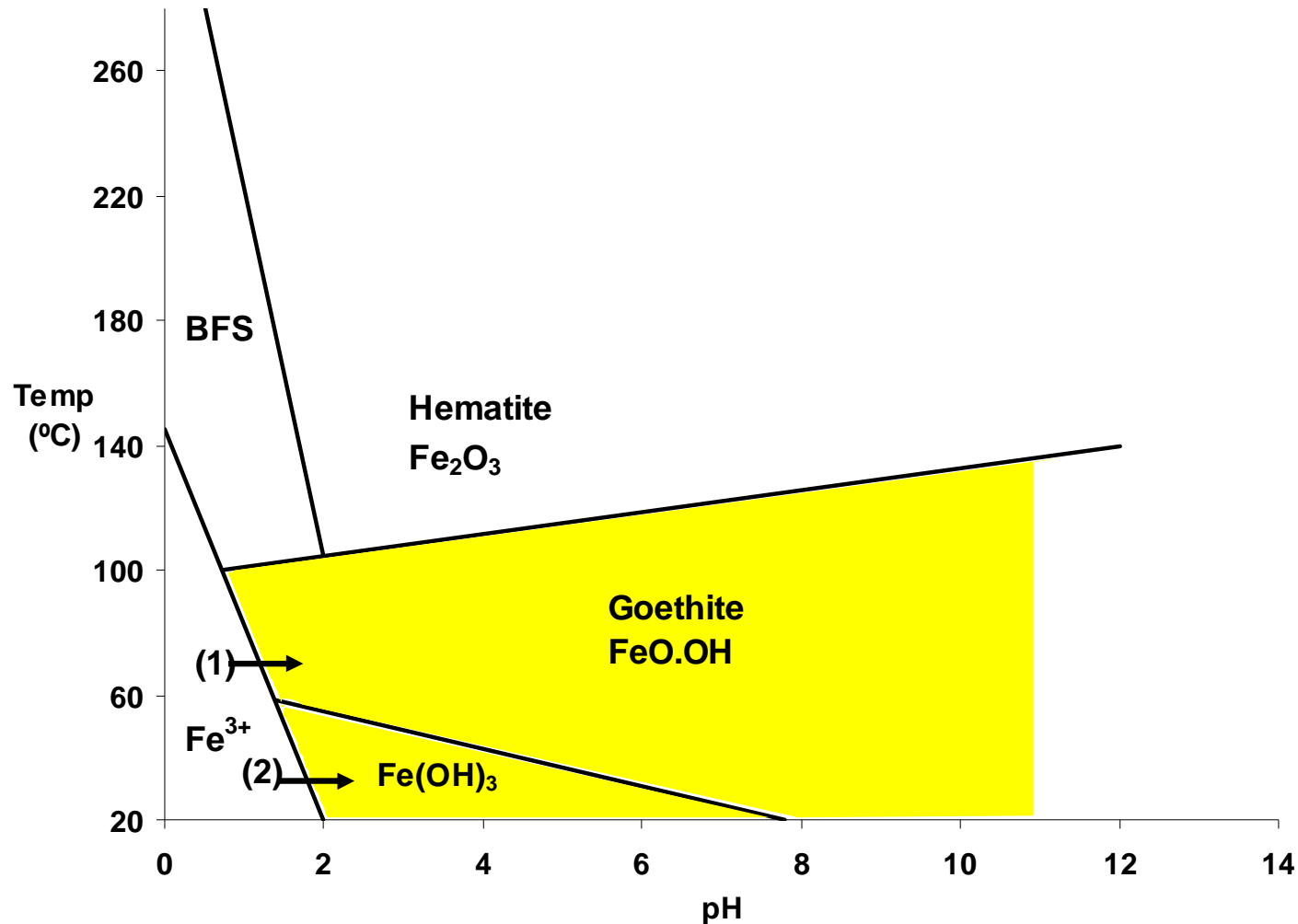
## THE HOT CURE PROCESS

Once the basic iron sulphate has decomposed to ferric sulphate, it can be separated from the solids by CCD or filtration, and neutralized with limestone

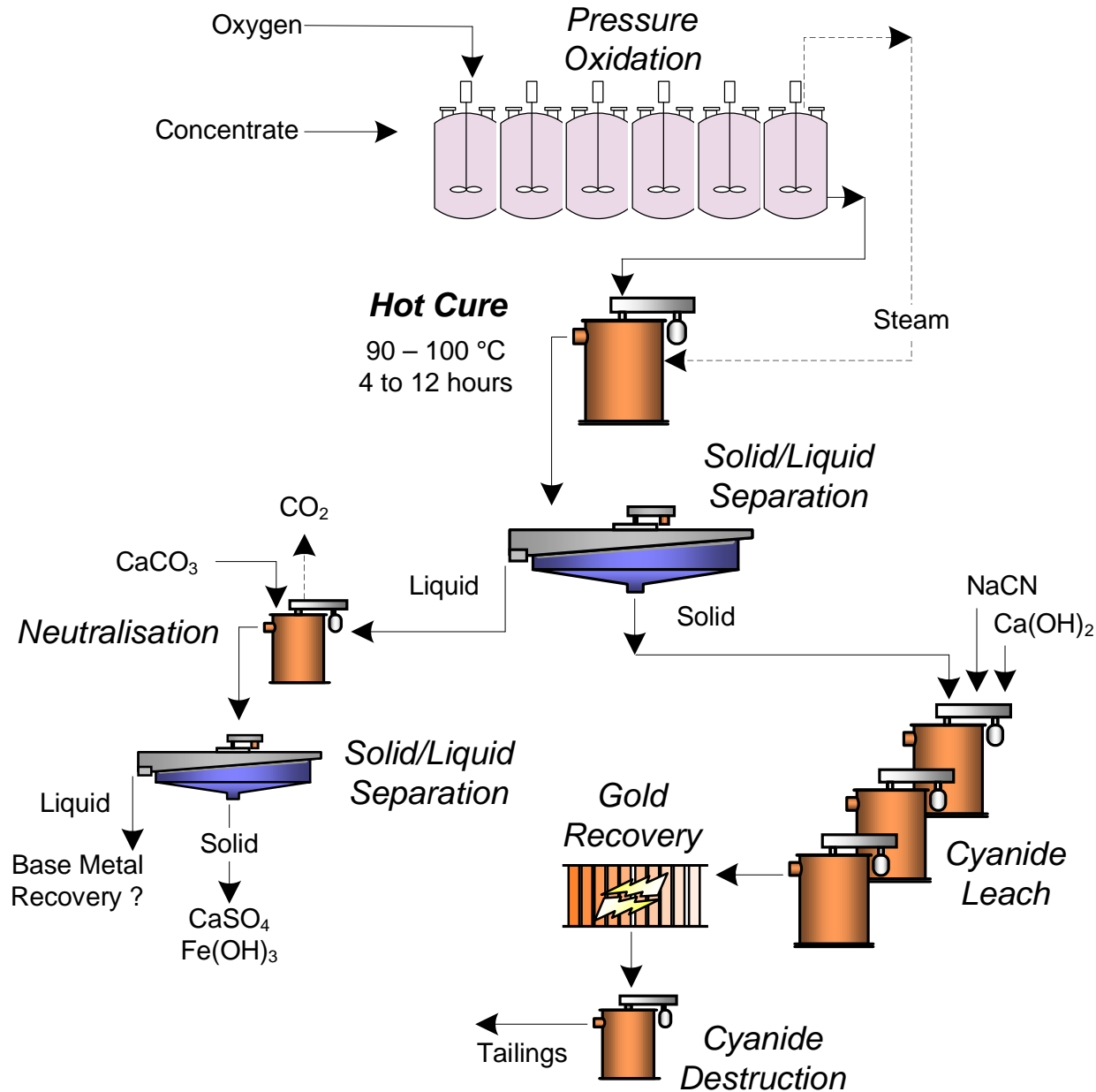




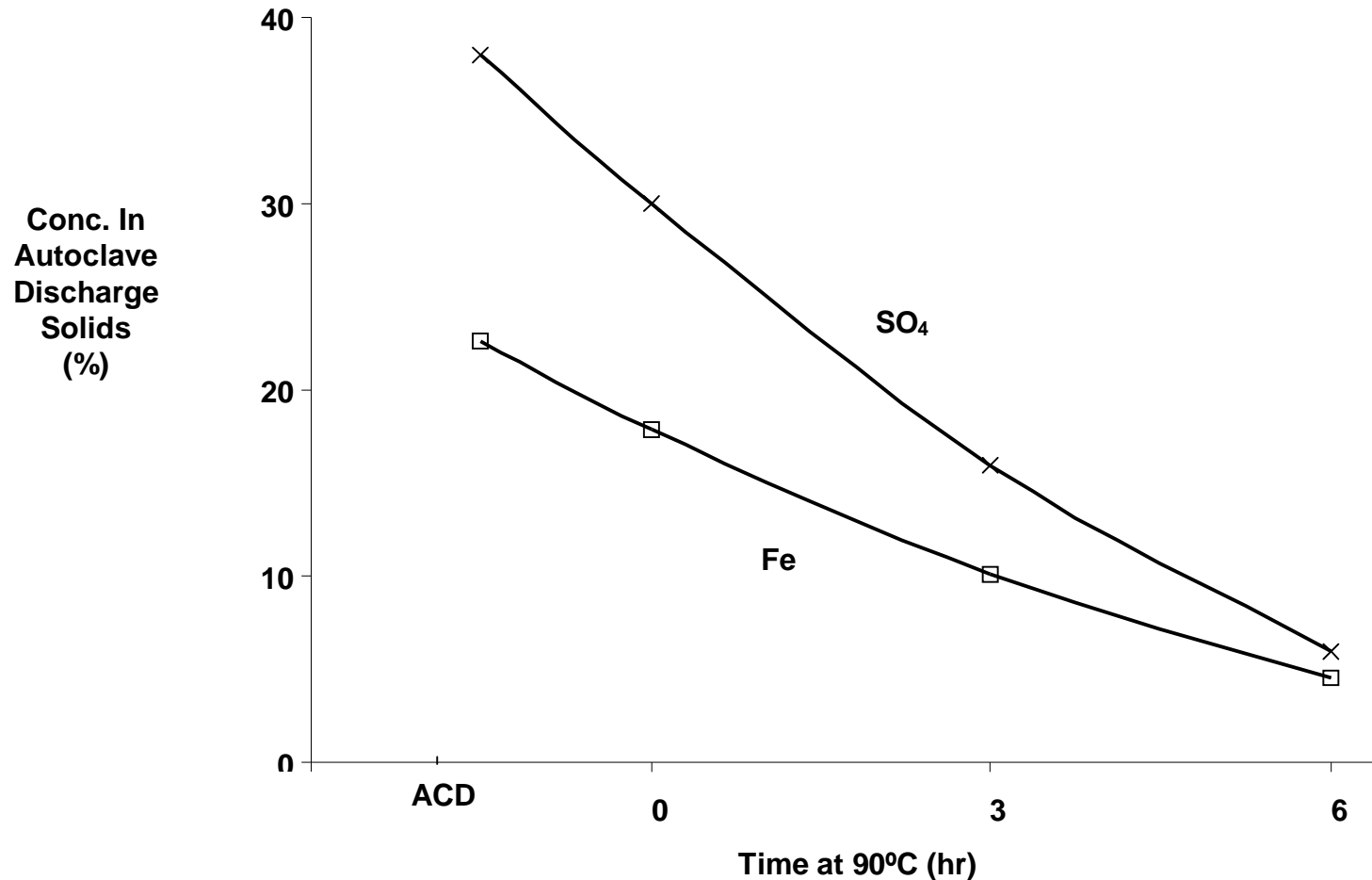
# NEUTRALIZATION OF THE ACID AND SULPHATE WITH LIMESTONE



# A REFRACTORY GOLD POX FLOWSHEET INCORPORATING HOT CURING



# QUIMSACOCHA PROJECT, ECUADOR (IAMGOLD CORPORATION)



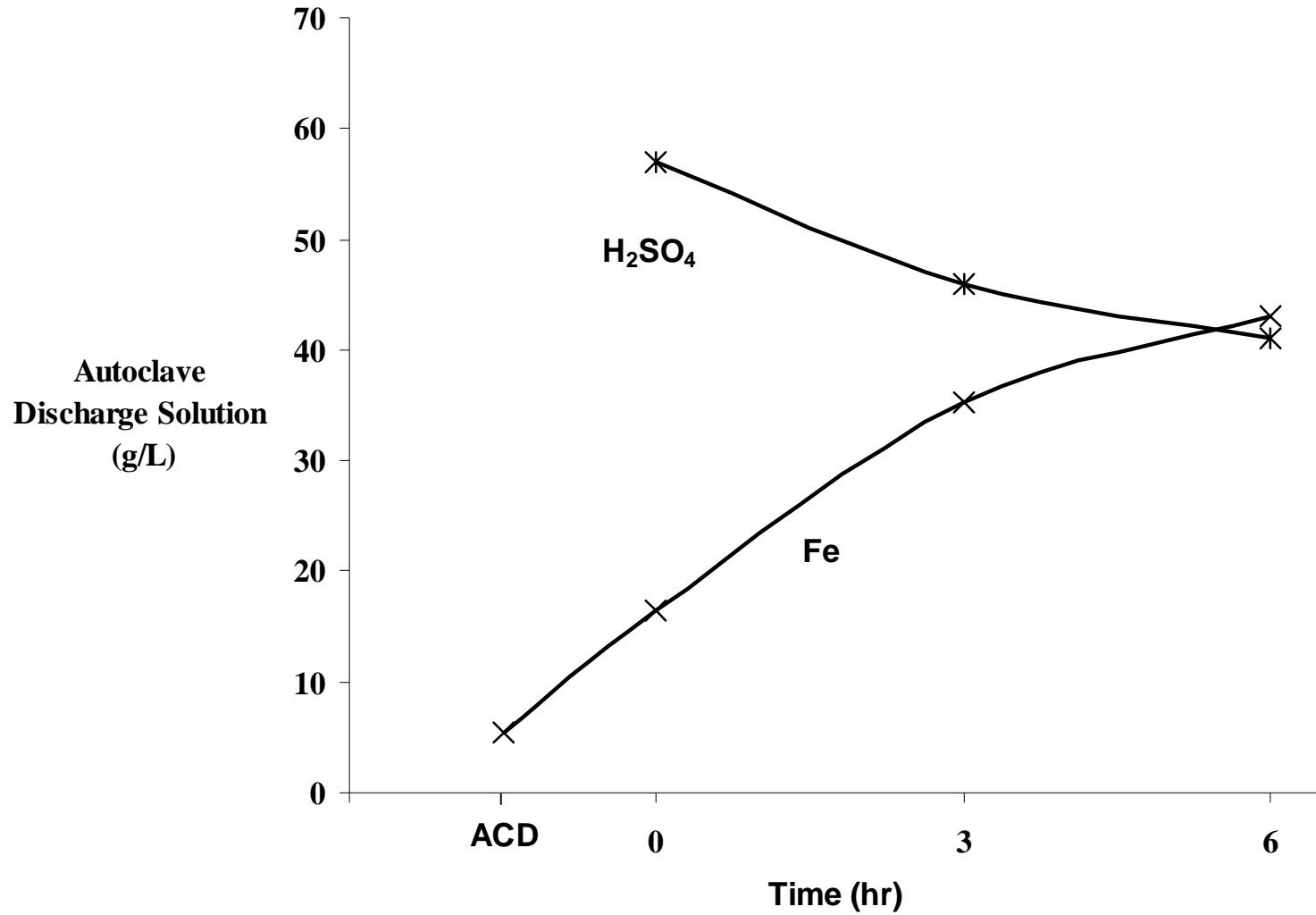
$$\Delta\text{Fe (mass/mass)} = 18.1\%$$

$$\Delta\text{SO}_4 \text{ (mass/mass)} = 32.0\%$$

$$\text{Fe/SO}_4 = 0.57$$



# QUIMSACOCHA PROJECT



# QUIMSACOCHA PROJECT

Concentrate head grade: 24 g/t Au, 104 g/t Ag

<u>PRODUCT</u>	<u>RECOVERY</u>		<u>ALKALI CONSUMED</u>		<u>APPROX. COST</u>
	Au %	Ag %	CaCO <sub>3</sub> kg/t	Ca(OH) <sub>2</sub> kg/t	\$/t
Autoclave Discharge	99.6	94.8	370	260	43
Hot Cure Discharge	99.4	91.9	704	15	9

