Processing of inorganic sludge into Water Treatment Chemicals from Industrial Effluents

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Precipitated calcium carbonate

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Waste gypsum

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$BaSO_4$ sludge

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Zambia

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Berkeley Pit, Butte,Motana

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Estimated Rate of Pumping Required

Basin	Pumping rate (Ml/day)
Far	65
Western	60
Western Central	100
Eastern	120+
Total for Gauteng gold mines	**345+**
Mpumalanga coal mines	**80+**

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Decant Point in Krugersdorp

SA 2006: Game Reserve, put at risk

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Formation of acid mine drainage

Rich in pyrite (FeS_2)
Generate acid when exposed to air and water

$$2FeS_2 + 7O_2 + 2H_2O \Rightarrow 2FeSO_4 + 2H_2SO_4$$

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Water quality of decant water

Parameter	**Feed** *(mg/l)*	**Treated** *(mg/l)*	**Recommended**
pH	3.1	7.5	
Sulphate	4510	250	500
Chloride	37	37	200
Free acid	500	0	
Sodium	96	95	150
Potassium	3	4	
Magnesium	113	2	
Calcium	559	30	
Silica	36	6	
Manganese	174	1	1
Iron(II)	1100	0	1
Iron(III)	200	0	0
Aluminium	6	0	1
Zinc	11	0	0.05
Nickel	18	0	0.01
Cobalt	7	0	0.01

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Sulphur wastes

- Acid and sulphate-rich effluent
- SO_2 and H_2S-rich gasses
- Waste gypsum

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Water quantities

- Rand Water treats 3700 Ml/d
- 360 Ml/day of polluted excess mine water is pumped to surface to prevent flooding of gold reserves.
- Polluted water impacts on South Africa's Gauteng Province, which generates 9% of total African Continent's GDP
- Similar problems from coal & other mines at various sites in Africa.

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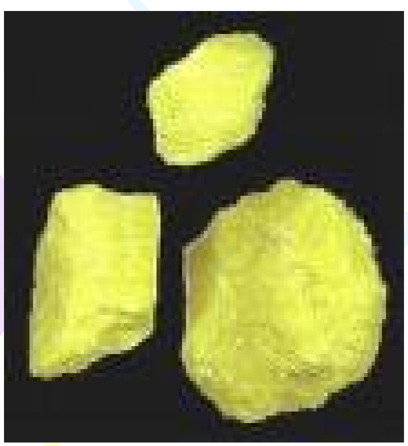
Sulphur demand

- As far as the supply and demand situation for sulphur is concerned, Africa is the major importer of sulphur

- Neighboring countries like Zambia and the DRC are importing large volumes of sulphur to make sulphuric acid for exploiting oxidised ores



Sulphur demand

- SA consumption of sulphur in all forms in 2002 was 1 080 000 t/a of which 700 000 t were imported

- In South Africa the fertilizer industry is by far the largest consumer of sulphur

- Demand is expected to increase in line with increased fertilizer usage and exports in SA

- Prospects for sulphur are positive with an increasing world-wide demand.

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CSIR developed technologies

Biological Sulfate Removal

- Using common substrates
- Using cheap substrates (grass)

Barium process for sulphate removal

- Barium sulphide
- Barium carbonate

Acid Water Neutralization

- Using lime
- Using limestone

Gypsum to Sulfur

- GypSLiM process (waste to valuables)

DesEl

- Capacitive De-Ionization

Fluoride Removal

- Using alumina (Al_2O_3)

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Comparison between alkalis

Lime	Limestone ($CaCO_3$)
High cost (R950/t) (R827/t as 100% $CaCO_3$)	Low cost (R220/t) (R314/t as 100% $CaCO_3$)
Lime slaker needs maintenance	No lime slaker
Accurate dosage required	No accurate dosage required
Unsafe to handle	Safe to handle

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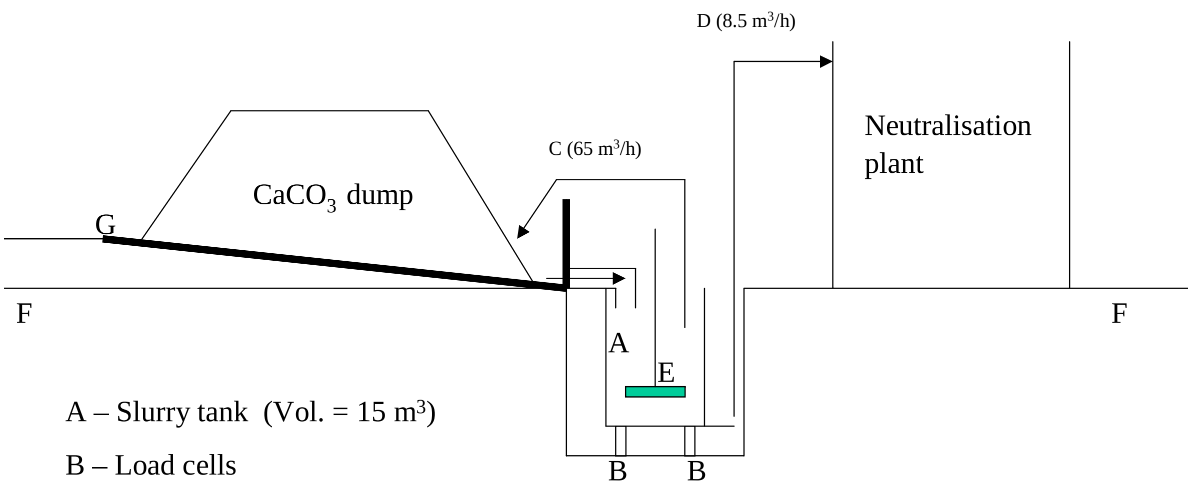
Schematic representation of limestone makeup and dosing system



A – Slurry tank (Vol. = 15 m^3)

B – Load cells

C – Recycle pump

D – Feed pump

E – Stirrer

F – Ground level

G – Concrete slab/wall (250 m^2)

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Water quality of Discard leachate

Parameter	Feed	Treated
pH	2.5	6.5
Acidity	11 000	200
Iron	4 000	<100
Sulphate	13 000	2 500
Alkalinity	-	120

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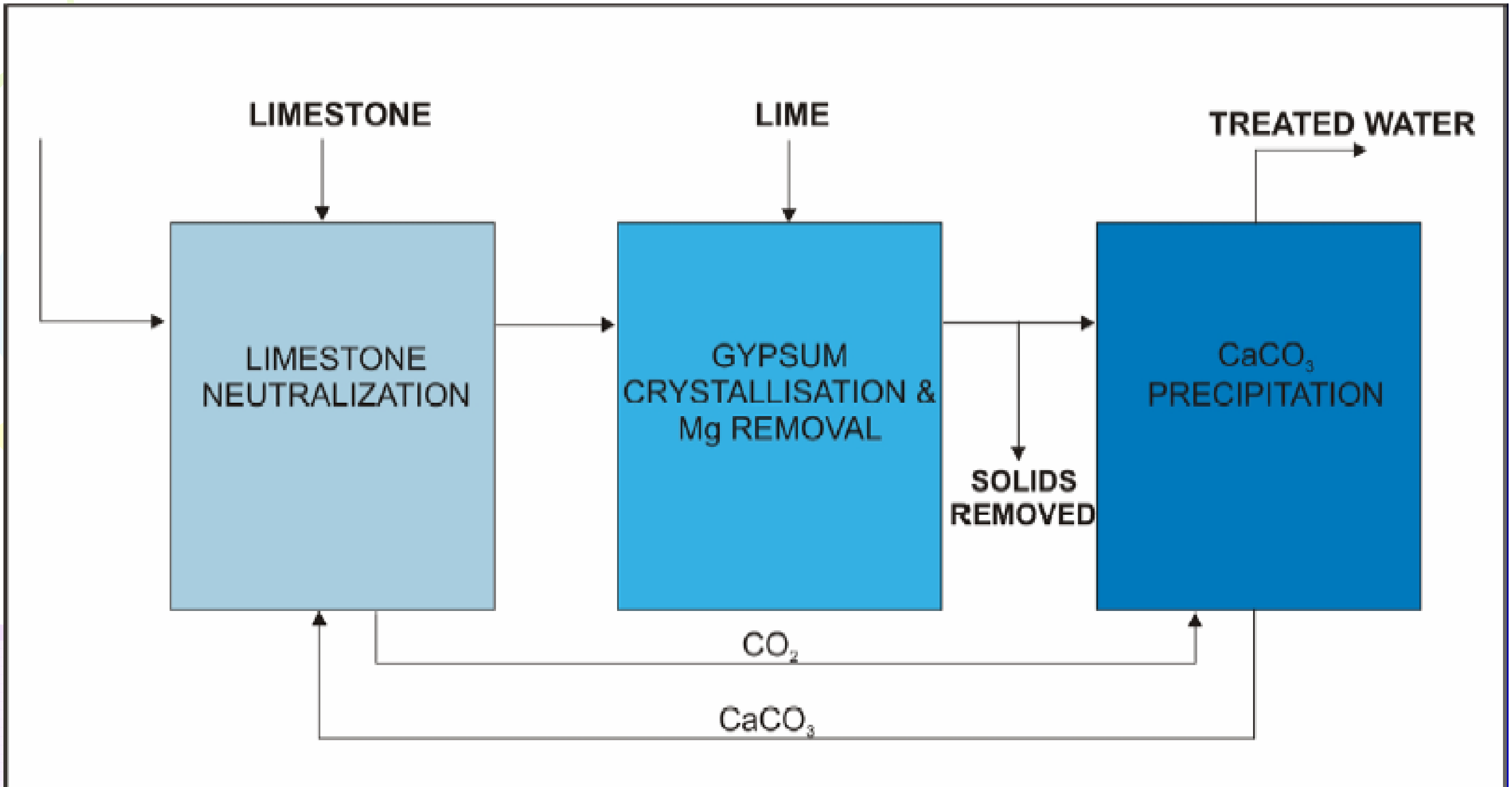
Limestone Neutralization



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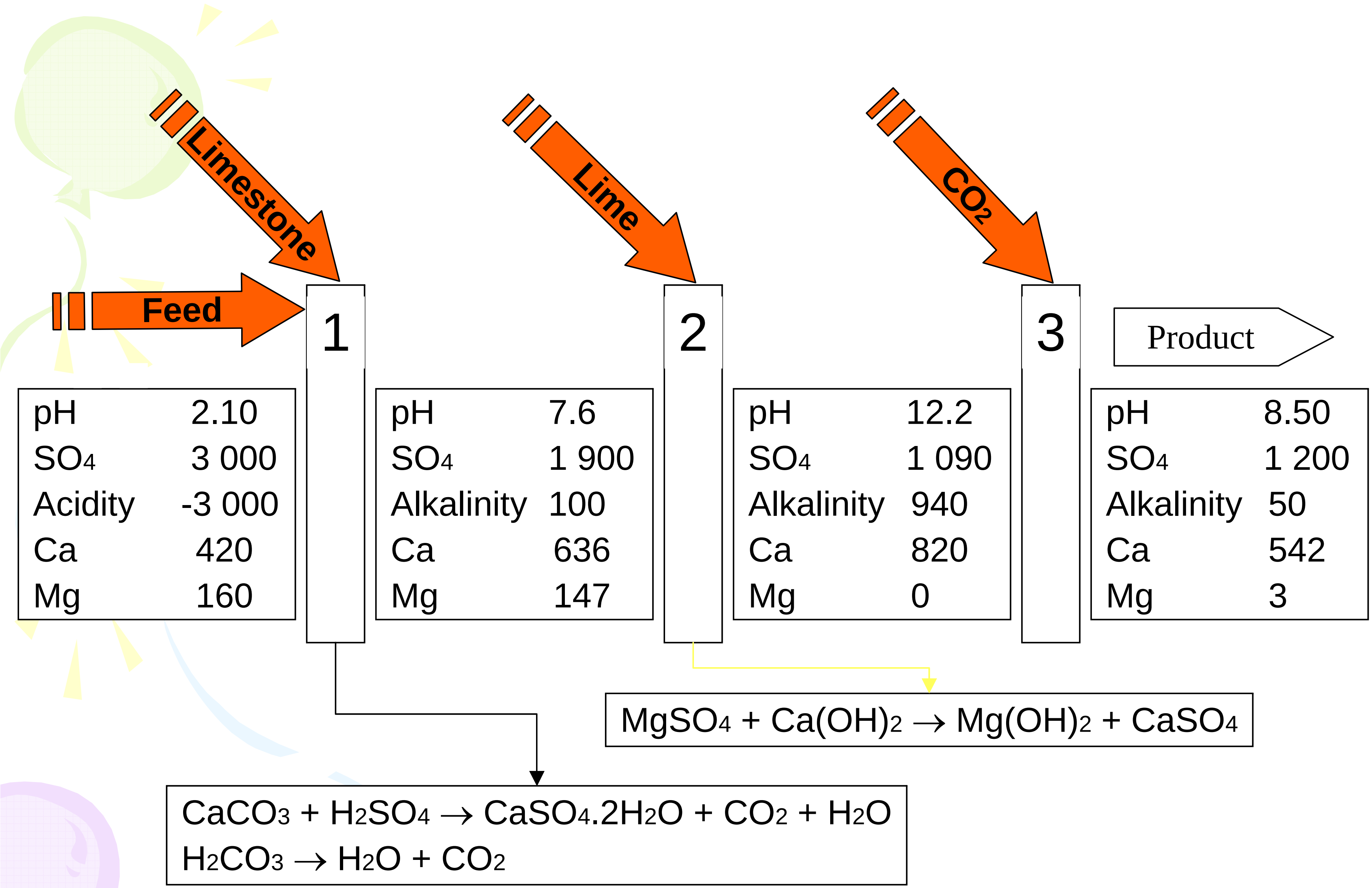

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Limestone/Lime Neutralisation Process Benefits

- Partial desalination
- Reduction in scale forming potential
- Recovery and re-use of process byproducts
- Simple to operate and maintain
- Cost effective compared to other partial desalination options (up to 50% cost savings)

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Namakwa

Iluka Resources, Hamilton

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Sulphate removal with barium process

$$BaCO_3 + SO_4^{2-} \longrightarrow BaSO_4 + CO_3^{2-} \quad (1)$$

- $BaSO_4$ has low solubility hence precipitates out of the solution
- The presence of Ca^{2+} in the feed leads to the formation of CaCO3

$$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3 \quad (2)$$

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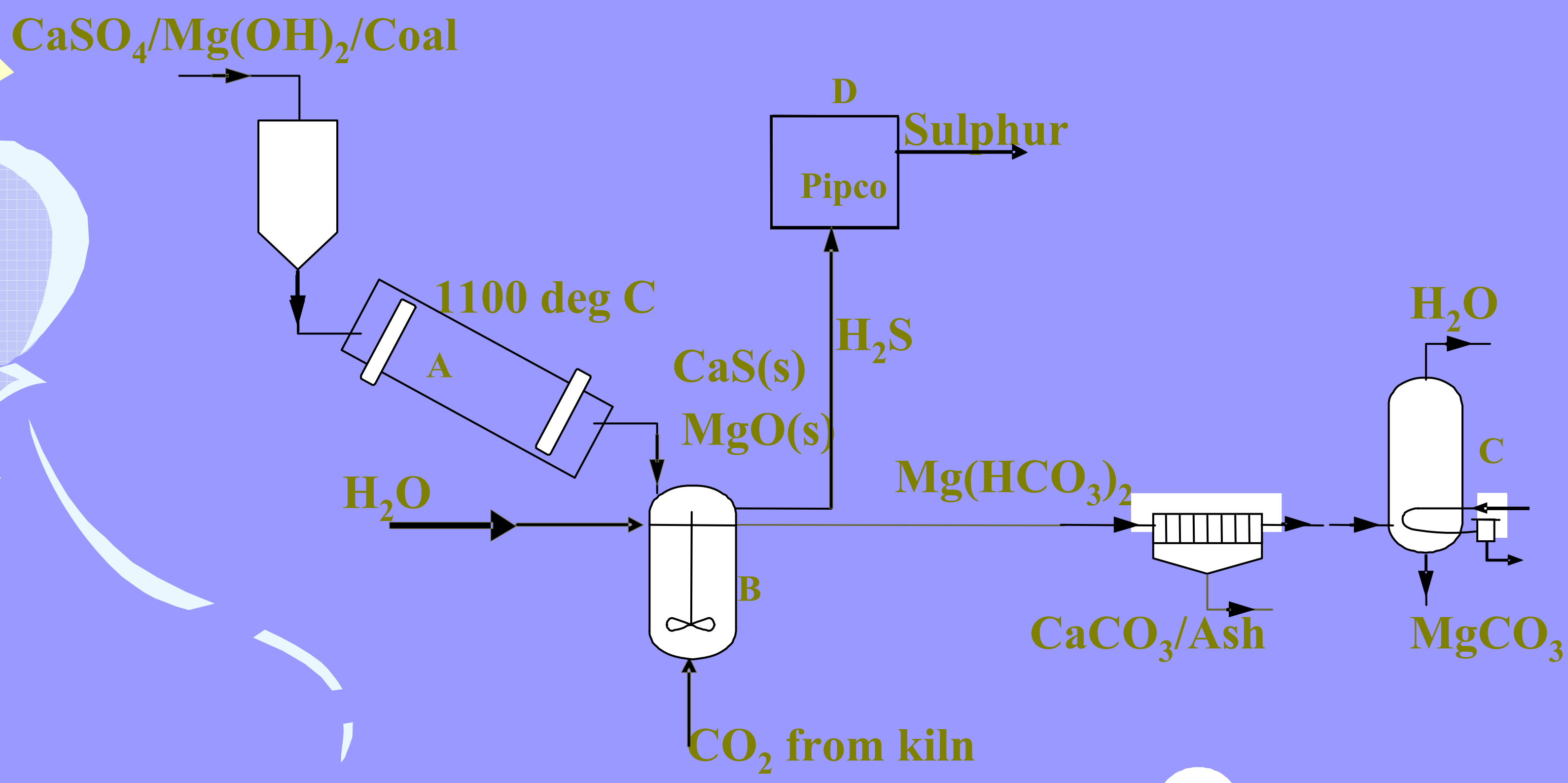
Sulphur Recovery flow diagram



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Sulphur Recovery Stages & Reactions

$CaSO_4(s) + 2C(s) \rightarrow CaS(s) + 2CO_2(g)$

Dissolution and Stripping of Sulphide

$2CaS\ (s) + 2H_2O(aq) + 2CO_2(g) \rightarrow 2CaCO_3(s) + 2H_2S\ (g)$

H_2S converted to Sulphur via the PipCo process

$2H_2S\ (g) + SO_2\ (g) \rightarrow 3S\ (s) + 2H_2O\ (aq)$

Reduction roasting of gypsum to form CaS

$Mg(OH)_2 \rightarrow MgCO_3$

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studies

Exp. number	Parameter	Value	% Gypsum converted to CaS
1	Time (min)	5 20 60	45 96 93
2	Temperature (°C)	900 1000 1100	35 80 96
3	$C/CaSO_4$ mole ratio	0 0.5 1 2 3	0 12 28 97 94
4	Particle size of Gypsum (µm)	38 63 125	90 56 19

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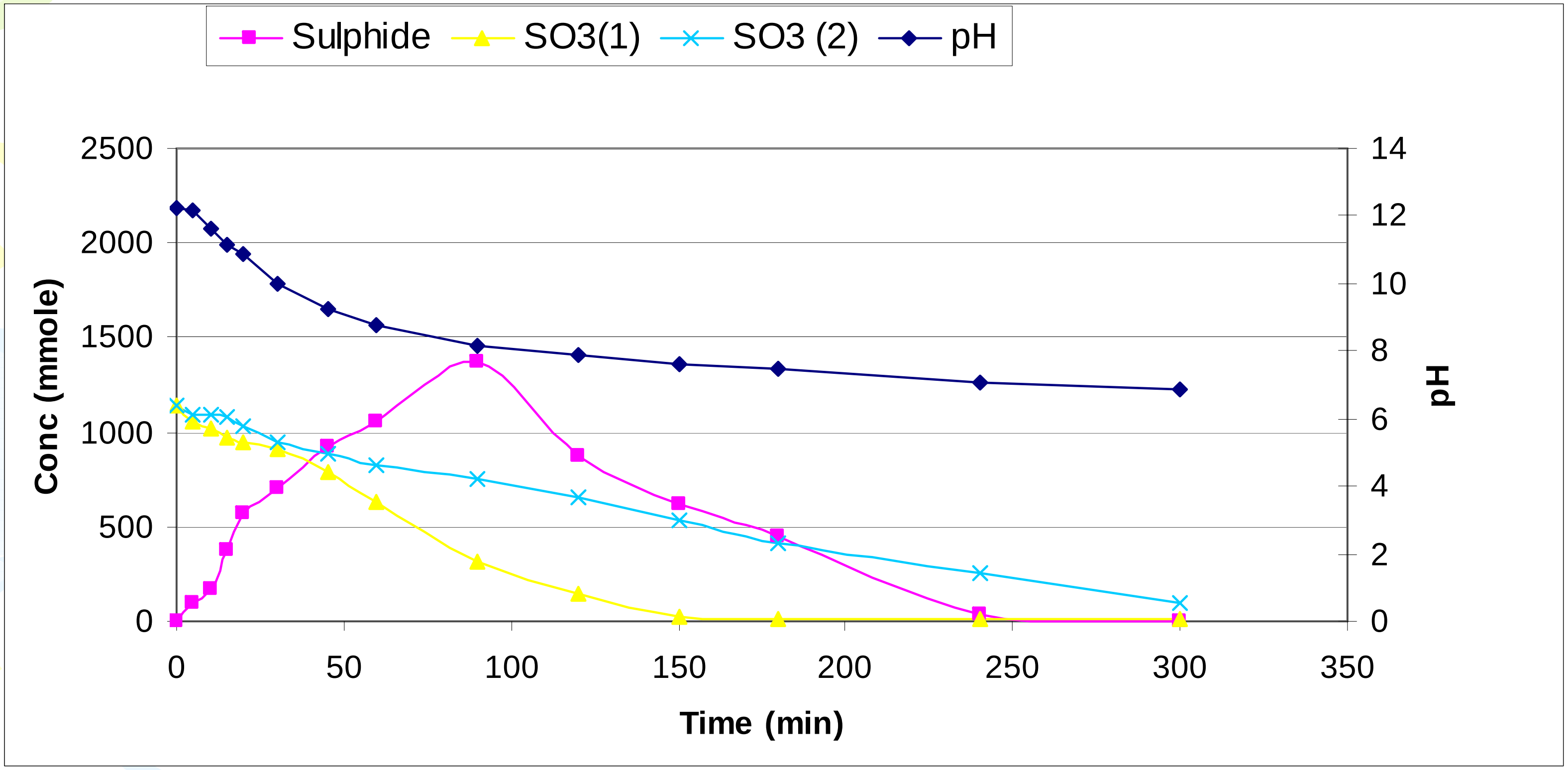
Results of the sulphide stripping with CO_2 (concentrations versus time)



$2CaS + H_2O + CO_2 \rightarrow CaCO_3 + Ca(HS)_2$ (12)

$Ca(HS)_2 + H_2O + CO_2 \rightarrow CaCO_3 + 2H_2S$ (13)

$CaS+2H_2O+2CO_2 \rightarrow Ca(HCO_3)_2+H_2S$ (14)

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Integration of various treatment processes

- Limestone neutralization
- Lime treatment
- Sulphate removal
- Metal removal with sulphide
- Sludge processing

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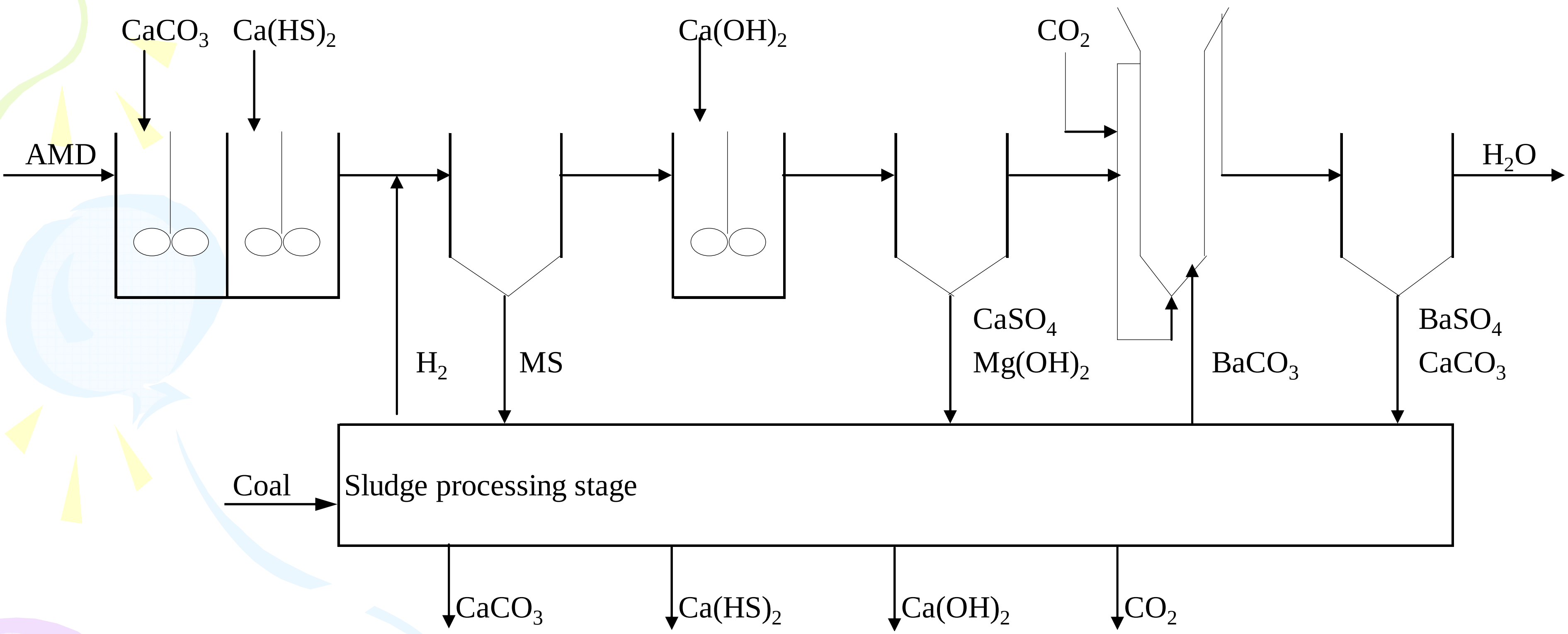
Integrated limestone / sulphide process



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Water quality

Parameter	Quality						
	Feed	**$CaCO_3$**	**CaS**	**Lime**	**CO_2**	**$BaCO_3$**	**SO_4**
pH	2.9	5.8	6.8	10.9	8.4	8.5	8.3
Sulphate (mg/l SO_4)	4870	4710	4500	2300	2310	85	200
Chloride (mg/l Cl)	37	37	37	37	37	37	37
Alkalinity (mg/l $CaCO_3$)	0			300	60	65	63
Acidity (mg/l $CaCO_3$)	800	100	50				
Sodium (mg/l Na)	50	50	50	50	50	50	50
Magnesium (mg/l Mg)	147	148	146	10	10	10	10
Calcium (mg/l Ca)	613	920	1580	1040	948	10	70
Barium (mg/l Ba)						40	0.4
Manganese (mg/l Mn)	46	46	4.8	1			
Iron(II) (mg/l Fe)	949	949	11	0.01			
Iron(III) (mg/l Fe)	35	0	0	0			
Aluminium(III) (mg/l Al)	26.4	0.5					
Cobalt (mg/l Co)	5	5	0.06				
Nickel (mg/l Ni)	18	18	0.14				
Zinc (mg/l Zn)	11.9	11.9	0.15				
TDS (mg/l)	7592	6993	6378	3660	3399	280	414
Cations (meq/l)	102.5	99.2	94.8	55.0	50.4	4.1	6.5
Anions (meq/l)	102.5	99.2	94.8	55.0	50.4	4.1	6.5

Note: Ca and SO4 values were adjusted to obtain ion balance.

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Valuable products:

- Drinking water
- Sulphur
- $CaCO_3$
- $MgCO_3$
- Metals

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Research supported by SA Government's Technological Human Resources Industrial Programme (THRIP)

- Industrial partners
- Higher qualifications
- Good science (Publications, Patents)
- SMME (Small Medium and Micro Enterprises)
- BEE (Black Empowerment Enterprise)

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