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COAL MINE ACID MINE DRAINAGE TREATMENT AND SLUDGE PROCESSING

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SUMMARY

In this study a modified CSIR alkaline barium calcium (ABC) process consisting of a water treatment stage and a thermal process stage, was evaluated on coal mine acid mine drainage (AMD). The AMD treatment went through the following treatment stages; neutralization using calcium hydroxide (pH 8), metal removal using H_2S, magnesium removal using calcium hydroxide (pH 12) and sulphate removal using barium carbonate. The simulated barite/calcite sludge prepared in the laboratory using commercial reagents was subjected to a thermal process in the presence of carbon. The study indicated that gypsum formation can be reduced by 80 % during the water treatment stage, thereby reducing the amount of gypsum that needs to be processed using the costly GypSLim process to 20 %. Temperature, reaction time, carbon/barite molar ratio, calcite/barite molar ratio and feed PSD were shown to have an effect on the thermal processing of the barite/calcite sludge. The capital and running cost estimate of the CSIR ABC process is included as Appendix A in this report.

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1.0 INTRODUCTION

The search for sulphate removal technologies from sulphate rich water has led to the development of the CSIR alkali barium calcium (ABC) process. In this process, $BaCO_3$ is effectively used for the removal of sulphates from sulphate rich industrial waste waters via precipitation of barite, and have exhibited a number of advantages over the use of other chemicals (Maree JP et al. 2004; Hlabela et al, 2007). The precipitation of barite is favoured due to the low solubility of barite in water (0.0015 g/L). However, the use of $BaCO_3$ in mine water treatment for sulphate removal results in the production of large amounts of barite sludge. Besides its numerous existing uses, barite can also be thermally processed back to barium sulphide, which then can be used as a starting material for the production of $BaCO_3$, thereby increasing the viability of the overall process and reduce environmental pollution.

The current ABC process makes provision for two sludge processing stages, the barium sludge processing to recover $BaCO_3$, $Ca(OH)_2$ and sulphur as well as the gypsum sludge processing to recover $CaCO_3$, $MgCO_3$ and sulphur. The modified ABC has been designed to minimize the gypsum generation, thereby reducing the quantity of gypsum crystallized during the water treatment stage with all the sulphate removed as barite. This design increases the sludge load to the barium sludge processing stage, significantly reducing the gypsum sludge processing whose CAPEX alone is estimated at about R1 billion.

In this study the modified CSIR ABC process was evaluated on coal mine AMD from the neutralization stage to the thermal reduction stage. In this regard, AMD from Anglo coal was treated using the modified CSIR ABC process given in Figure 1. The AMD treatment went through the following treatment stages; neutralization using calcium hydroxide (pH 8), metal removal using H_2S, magnesium removal using calcium hydroxide (pH 12) and sulphate removal using barium carbonate. The barite/calcite sludge generated by this process was simulated using commercial reagents and thermally processed at high temperatures in the presence of carbon.

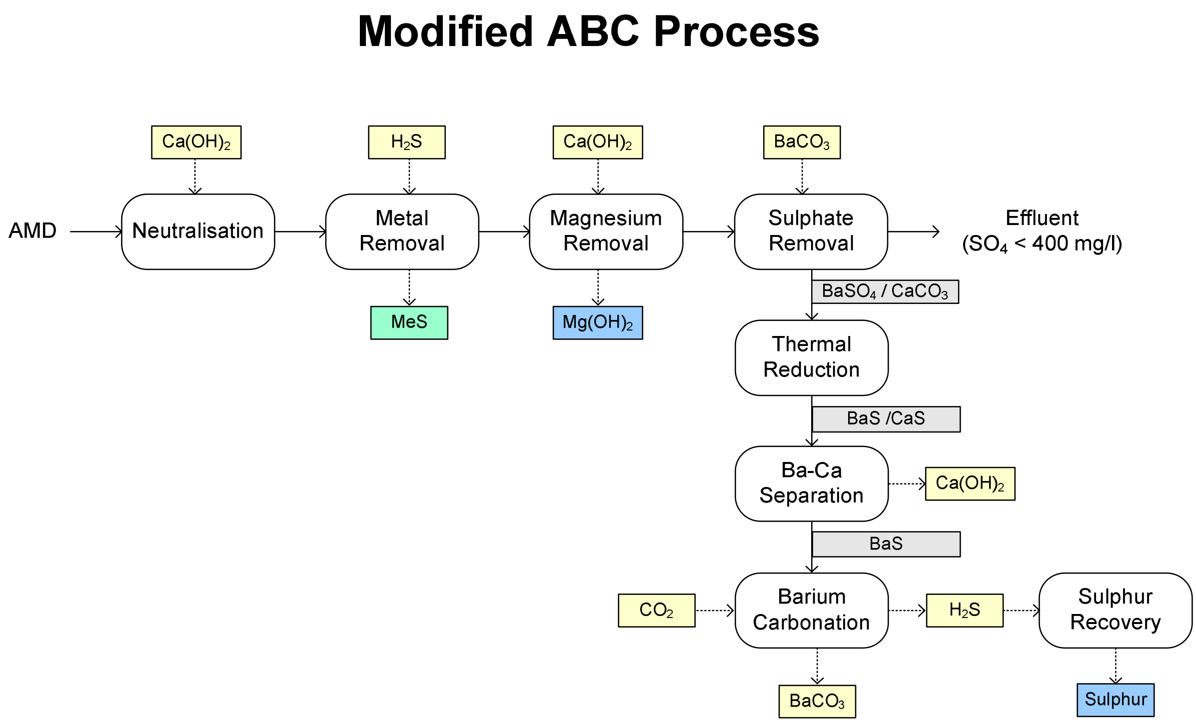


Figure 1. Modified Alkali Barium Calcium (ABC) process

2.0 MATERIALS AND METHODS

2.2 EXPERIMENTAL

2.2.1 Feedstock

AMD collected from Witbank (Anglo Coal) was used as feed water in the water treatment stage. Industrial grade $Ca(OH)_2$ was used for AMD neutralization and magnesium removal. A 99 % purity H_2S gas was used to precipitate metals as metal sulphides. Sulphate removal was carried out using synthetic $BaCO_3$. A mixture containing commercial grade barite and calcite as well as coal samples collected from George, Exxaro and commercial charcoal were used as feed material for the thermal studies.

2.2.2 Equipment

Batch experiments on coal mine AMD were conducted in 3 L completely stirred tank reactors (CSTR) equipped with a 6 paddle stirrer. The barite/calcite/coal thermal processing was conducted in a 150 mm quartz boat heated using an Elite tube furnace.

2.2.3 Experimental procedure

Batch studies on coal mine AMD treatment were carried out by neutralization using calcium hydroxide (pH 8), metal removal by hydrogen sulphide sulfidation, magnesium removal using calcium hydroxide (pH 12) and sulphate removal using barium carbonate. The thermal processing of the barite/calcite sludge was conducted by adding the sludge sample into a quartz boat, placing the boat into the tube furnace and heating the sludge in the presence of coal.

2.3 Experimental programme

The following aspects as given in Figure 2 were investigated in the water treatment stage, prior to sludge thermal processing;

2.3.1 Coal mine AMD treatment

- AMD neutralization using lime (pH 8)
- Heavy metal precipitation using H_2S gas as sulfidation agent
- Magnesium removal using lime (pH 12)
- Sulphate removal using $BaCO_3$

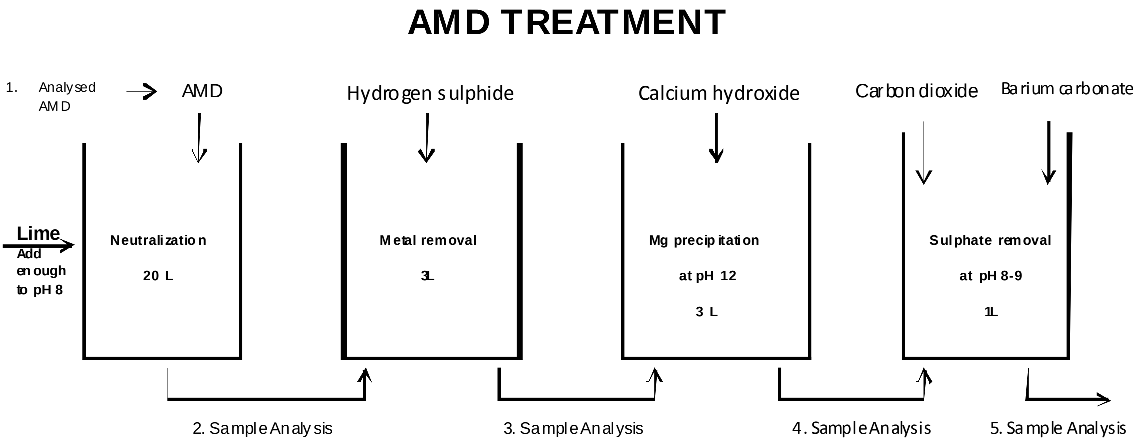


Figure 2. Coal mine AMD treatment

2.3.2 Thermal processing of barite/calcite sludge

- Effect of temperature: 1:1:2 mixture for a 15 min reaction time
- Effect of reaction time: 1:1:2 mixture using optimum temperature
- Effect of carbon/$BaSO_4$ ratio: 1:1 mixture using optimum temperature and reaction time
- Effect of calcite/barite molar ratio using optimum temperature, reaction time and carbon quantity
- Effect of feed PSD using optimum barite/calcite molar ratio, optimum temperature, reaction time and carbon quantity

2.4 Analytical procedure

Coal mine AMD feed water and samples collected at various stages during the water treatment process were filtered through Whatman No. 1 filter paper, before analyzing for sulphate using a HACH spectrophotometer and metals ions (Ca^{2+}, Mg^{2+}, Ba^{2+}, Al^{3+}, Mn^{2+} and Zn^{2+}) using Inductively Coupled Plasma Spectroscopy (ICP). Solid samples collected during thermal studies were analysed for sulphide content following the iodometric method. These samples were also analysed by X-Ray Diffraction technique. For XRD analysis the samples were analyzed using a PANalytical X'Pert Pro powder diffractometer with X'Celerator detector and variable divergence- and fixed receiving slits with Fe filtered Co-Kα radiation on a back loading preparation method. The phases were identified using X'Pert Highscore plus software.

3.0 RESULTS AND DISCUSSIONS

3.1 Coal mine AMD treatment

Table 1 shows the acidity, alkalinity, sulphate and concentration of metals in the feed coal mine AMD, after neutralization, hydrogen sulfidation, magnesium removal and sulphate removal. Table 2 shows the change in the metal and sulphate concentration with pH during sulfidation over a period of 40 minutes. Figure 3 shows metals and sulphate concentrations as a function of pH while Figure 4 shows sulphate removal as a function of time.

Table 1. Coal mine AMD treatment using the CSIR modified ABC process

	Units	Feed	After neutralization	After H_2S sulfidation	After Mg removal	After SO_4^{2-} removal
pH		3.00	8.00	4.36	12.00	8.00
Acidity	mg/L $CaCO_3$	700	100	100	0	0
Alkalinity	mg/L $CaCO_3$	0	42	42	104	104
Sulphate	mg/L	3200	2700	2700	2700	100
Aluminium	mg/L	43	0.6	0.6	0.6	0.6
Calcium	mg/L	447	759	803	4420*	1870*
Copper	mg/L	0.13	<0.06	<0.06	<0.06	<0.06
Magnesium	mg/L	205	157	127	0.8*	2 *
Manganese	mg/L	25	2.5	2.5	2.3	2.3
Zinc	mg/L	2.5	-	-	-	-

*Indicates data incorporated from Table 2 after optimization of the H_2S sulfidation stage

From Table 1, it can be seen that the acidity drops from 700 mg/L $CaCO_3$ in the feed coal mine AMD to 100 mg/L $CaCO_3$ after neutralization to pH 8 using lime. The acidity remains at 100 mg/L $CaCO_3$ after sulfidation before it drops to zero upon magnesium removal using lime at pH 12. The alkalinity data also shows a clear correlation to the acidity data, with the feed initially recording an alkalinity of zero. This alkalinity rises to 42 mg/L $CaCO_3$ after neutralization using lime at pH 8, remains at 42 mg/L $CaCO_3$ after sulfidation, before rising to 104 mg/L $CaCO_3$ after magnesium removal at pH 12.

The sulphate concentration from Table 1 shows an interesting trend as the coal mine AMD is taken through the four treatment steps. The feed sulphate concentration of 3200 mg/L only reduces to 2700 mg/L after magnesium removal representing about 16 % loss in sulphate before sulphate removal as barium sulphate. Based on the sulphate content lost after magnesium removal, only 0.9 g of gypsum is capable of forming per every 1 L of coal mine water treated using the initial three steps described in the water treatment stage. The two neutralization steps in the traditional ABC process has been reported to reduce sulphate from 4870 mg/L to 2300 mg/L, representing a 53 % loss in sulphate (Motaung et al., 2008). Based on this, 4.60 g of gypsum is capable of forming per every 1 L of coal mine AMD treated using the traditional ABC water treatment process. In this regard, gypsum formation can be minimized by 80 % thereby reducing the amount of gypsum that needs to be processed by the costly GypSLim process to 20 %. From Table 1, there is significant removal of metals such as Al, Cu and Mn as metal hydroxides upon neutralization to pH 8. The residual metals that remain in the coal mine AMD are not significantly removed by sulfidation. The sulfidation data in Table 1 was generated using a low hydrogen sulphide flow rate over a sulfidation period of 10 minutes. Under such conditions of hydrogen sulphide flow rate and sulfidation time, metals failed to precipitate as metals sulphides probably due to the mass transfer limitations of hydrogen sulphide. As a result, a higher hydrogen sulphide flow rate (350 ml/min) over a longer sulfidation period (40 min) was used as pH was changed using lime to precipitate the metals as either metal hydroxides or metal sulphides as given in Table 2 and Figure 3.

Table 2. Sulfidation treatment at a hydrogen sulphide flow rate of 350 ml/min

pH of reaction mixture	2.45	2.69	3.17	4.36	5.1	6.06	7	8.09
Sampling Time (min)	0	5	10	15	20	26	33	40
Al	32	32	31	28	2.2	0.18	0.07	0.08
Cu	0.06	0.07	0.06	0.06	0.06	0.06	0.06	0.06
Mn	15	16	15	17	15	16	0.54	0.05
Ca	304	338	448	570	-	914	1610	3460
Mg	138	151	143	160	107	152	107	127
Zn	0.9	1.1	0.21	0.12	0.08	0.08	0.14	0.14
Sulphate	2200	2170	2140	2110	2080	2040	2010	2000

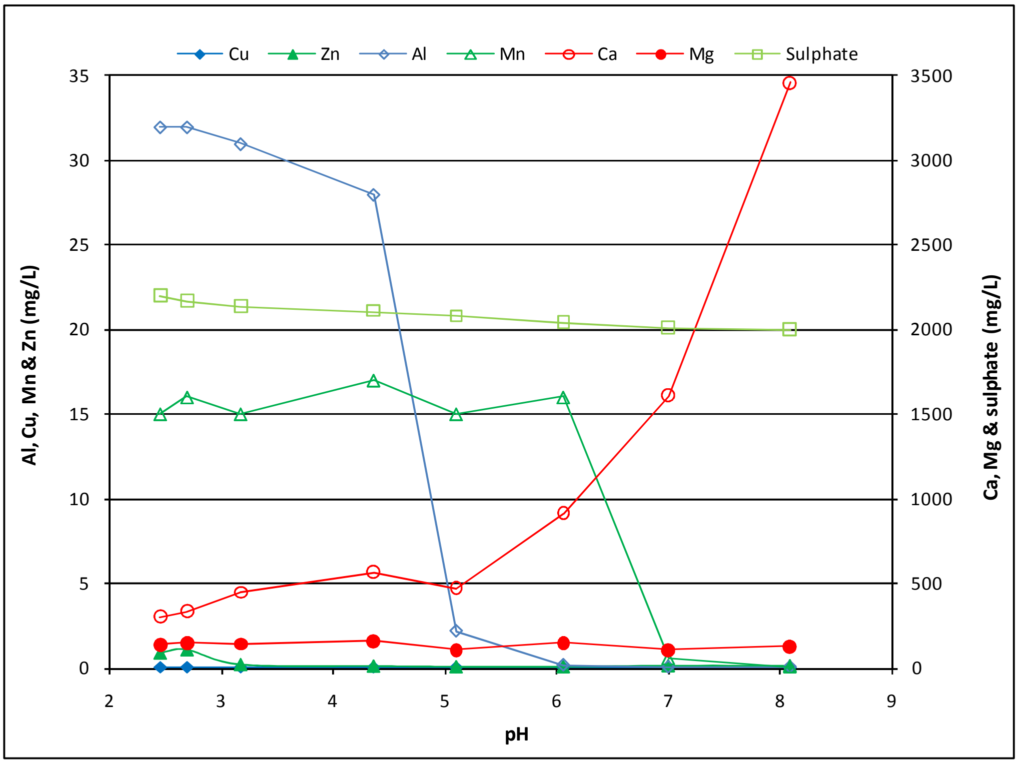


Figure 3. **Removal of metals by simultaneous neutralization and sulfidation from coal mine AMD**

It can be seen from Figure 3 that with the exception of calcium added as lime for pH control and magnesium, all metals are removed from the coal mine AMD within a pH range of 3.00-8.00 suggesting that the removal of these metals is pH dependent. In this regard, 93 % Al gets removed at pH 5.0, while 96 % Mn is removed at pH 7 and 87 % of Zn is removed at pH 4.36. Al is probably removed as a metal hydroxide, while Mn and Zn are removed as metal sulphides. The overall removal for both Al and Mn is 99.7 %. The magnesium concentration remains constant since its removal can only be effected at pH 12 during the magnesium removal step. From Figure 3 the extrapolated sulphate content data indicate that sulphate concentration at the end of the sulfidation process was 2000 mg/L representing a mere 9 % loss of sulphate to gypsum formation. This minimizes the sulphate available for gypsum formation and maximizes the sulphate that gets removed using barium carbonate as given in Figure 4, thereby generating most of the sludge as barium sulphate-calcium carbonate sludge for subsequent thermal processing.

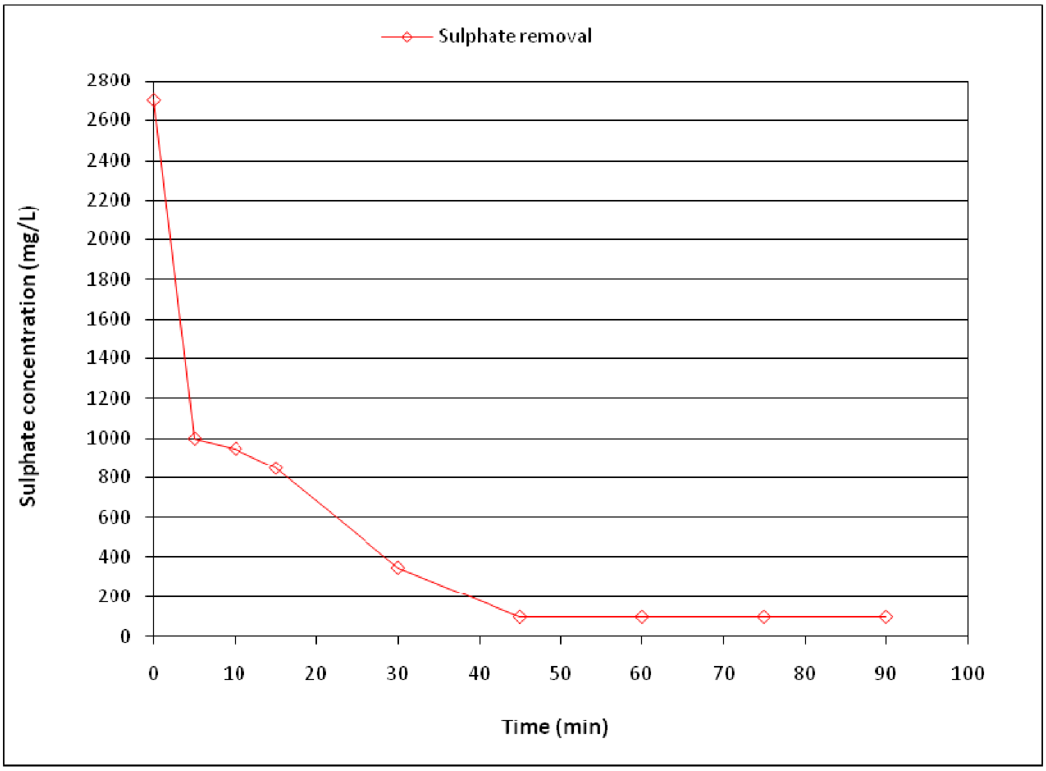


Figure 4. **Removal of sulphate from coal mine AMD**

The removal of sulphate via barium sulphate and calcium carbonate precipitation as given in Figure 4 shows that the sulphate that is kept in the coal mine AMD during the first three water treatment stages is removed from 2700 mg/L to less than 100 mg/L in less than 40 minutes. According to the South African National Standards (SANS) 241 Class I and Class II water standards, the recommended sulphate operational limit is less than 400 mg/L while the maximum allowable for a limited duration ranges from 400-600 mg/L. From Figure 4, sulphate gets removed to below the recommended operational limit.

In this regard, the sulphate removal step maximizes the barite-calcite sludge generation for subsequent thermal processing to recover barium carbonate and lime for reuse in the water treatment stages. Thermal processing of the barite-calcite sludge is discussed in more detail under section 3.2.

3.2 Thermal processing of barite/calcite sludge

Figure 5 shows the change in the Gibbs free energy with temperature for the main 3 reactions involved during thermal processing of a barite/calcite sludge as predicted by modelling. Figures 5-9 shows the effect of various parameters (temperature, reaction time, carbon/barite molar ratio, calcite/barite molar ratio and feed PSD) on the thermal processing of a barite/calcite sludge. The effect of these parameters on the thermal processing of the barite/calcite sludge have been evaluated in terms of the barium sulphide yield, degree of barite conversion and degree of calcite conversion.

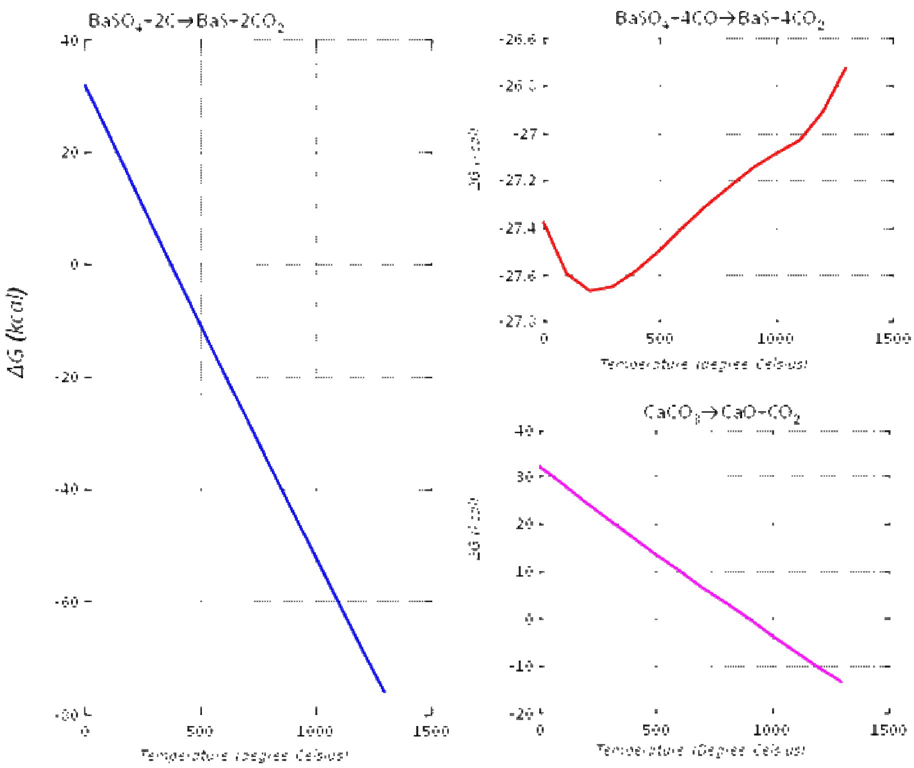


Figure 5. Gibbs free energy with temperature for the 3 main reactions during thermal process

The 3 main reactions involved in the barite/calcite sludge decomposition are given as follows;

$BaSO_4$ (s) + 2C (s) → BaS (s) + $2CO_2$ (g).. (1)

$BaSO_4$ (s) + 4CO (g) → BaS (s) + $4CO_2$ (g).. (2)

$CaCO_3$ (s) → CaO (s) + CO_2 (g).. (3)

From Figure 5, a linear relationship between the Gibbs free energy and temperature with a negative slope is observed for both barite and calcite thermal processing using coal as a reductant. For thermal processing of barite using carbon monoxide as reductant, a linear relationship with a positive slope is observed. As seen in Figure 5, the Gibbs free energy becomes more negative (thermodynamically favorable) at temperatures above 1000 ^{o}C, suggesting that the optimum thermal processing temperature for the barite/calcite sludge lies above 1000 ^{o}C. At a temperature of 1000 ^{o}C, the Gibbs free energies for thermal processing of barite using coal, carbon monoxide and calcite decomposition are predicted at -55 kcal, -27.1 kcal and -5 kcal respectively.

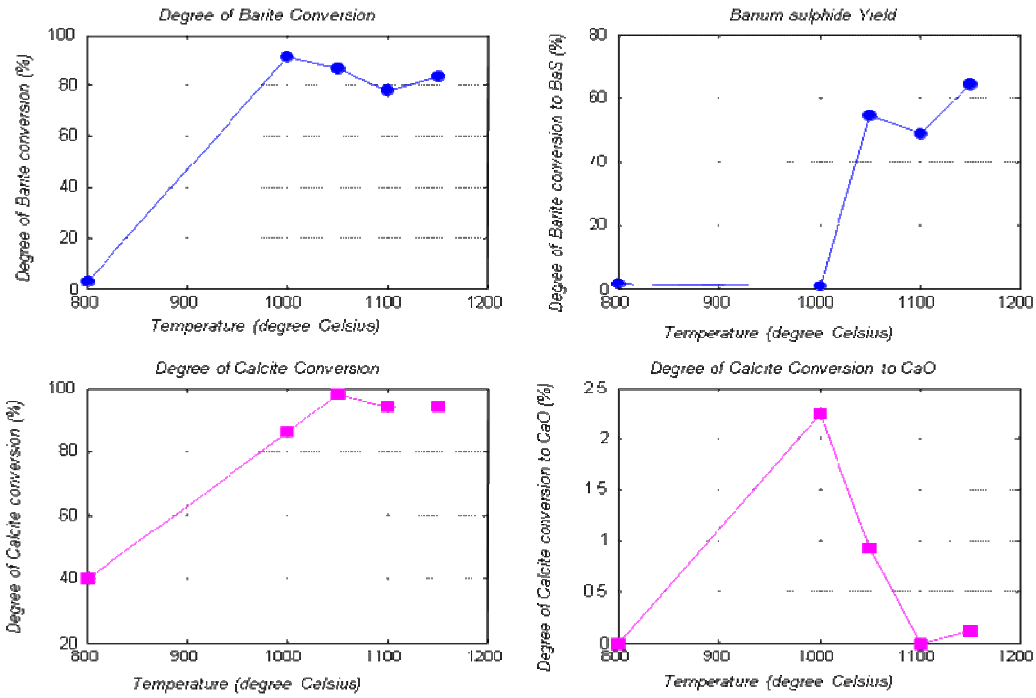
Based on this data, thermal processing of barite using coal is predicted to be thermodynamically more favorable compared to using carbon monoxide, while the decomposition of calcite to calcium oxide is least favorable.

From Figure 6a, it can be seen that the yield of barium sulphide is less than 2 % in the temperature range 800-1000 ^{o}C. The percentage conversion barite rises to more than 80 % within this temperature range. The barium sulphide yield improved dramatically when the temperature was increased to 1030 ºC and above. The highest barite conversion was recorded at a temperature of 1000 ºC. On the contrary the barium sulphide yield was very low at this temperature.

The degree of calcite conversion increases linearly to almost 100 % in the temperature range 800-1050 ^{o}C. Beyond this temperature, the calcite conversion remains constant. As predicted by the thermodynamics modelling given in Figure 5 for the Gibbs free energy data, a conversion of calcite to calcium oxide of less than 2.5 % is achieved at a temperature of 1000 ^{o}C. From Figure 2 (b), a significant portion of calcite is converted to calcium hydroxide (28 %) and calcium sulphide (45 %) at temperatures of 1100 ^{o}C and 1000 ^{o}C respectively. Moreover, a significant portion of barite (14 %) is converted to barium carbonate at a temperature of 1050 ^{o}C.

Based on Figure 6, the temperature is the driving force of the thermal reduction process, with the optimum temperature in the range 1030-1100 ^{o}C. Under optimum temperature, calcite is decomposed to approximately 20 % calcium hydroxide and 35 % calcium sulphide, while barite is reduced to about 60 %, 15 % barium carbonate and 10 % remaining unconverted.

(**a**)



(**b**)

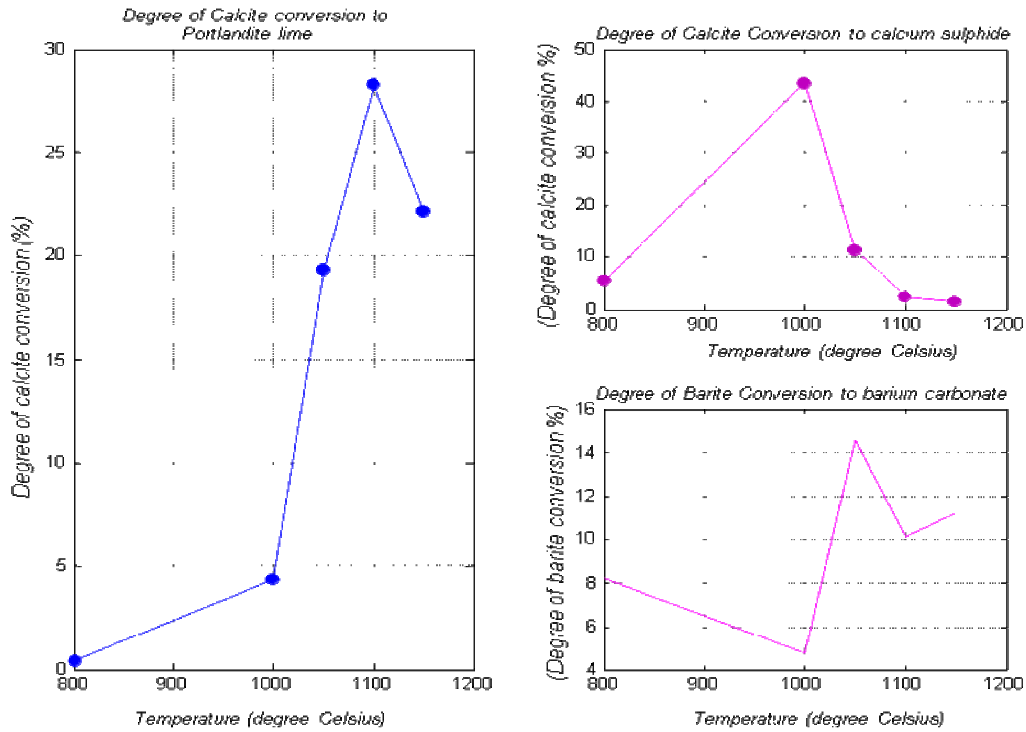
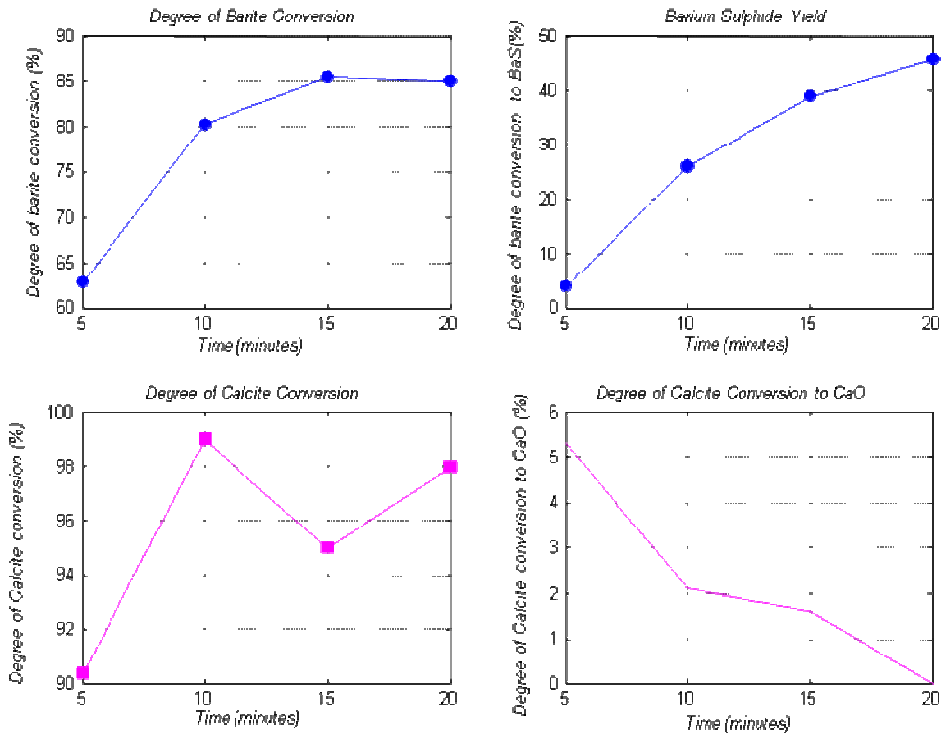


Figure 6. Effect of temperature- reaction time = 15 minutes; mass barite = 6 g (98% purity), mass calcite = 2.547 (99% purity) mass coal = 1.0086 g (60% purity)

(a)



(b)

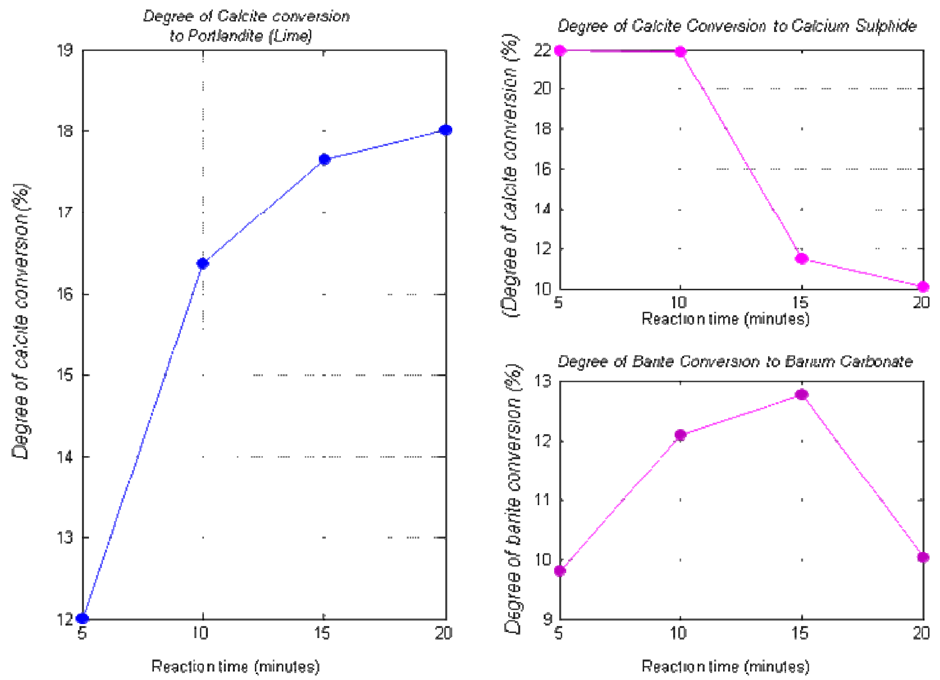


Figure 7. Effect of reaction time – temperature = 1030 °C; mass barite = 7.00 g (98% purity); mass calcite = 2.97 (99% purity) mass coal = 0.7845 g (60% purity)

From Figure 7, it can be seen that the barium sulphide yield, barite conversion and calcite conversion to lime increases with time. However, the barium sulphide yield did not reach a plateau and longer residence time would be required to improve the barium sulphide yield. Both the barite conversion and the calcite conversion to lime reach a plateau after 15 mins (85 % conversion) and 20 mins (18 % conversion) respectively. Despite a thermodynamically unfavourable Gibbs free energy as given in Figure 5, the rate of calcite decomposition is faster than the rate of barite reduction. In this regard, the later will determine the overall performance time during thermal processing of the barite/calcite sludge.

At a longer HRT in the kiln, the calcite conversion to calcium oxide and calcium sulphide yield decreases while more lime is formed. Therefore, the optimization to improve separation of barium sulphide from the other calcium compounds in the next stage could be based on this criterion.

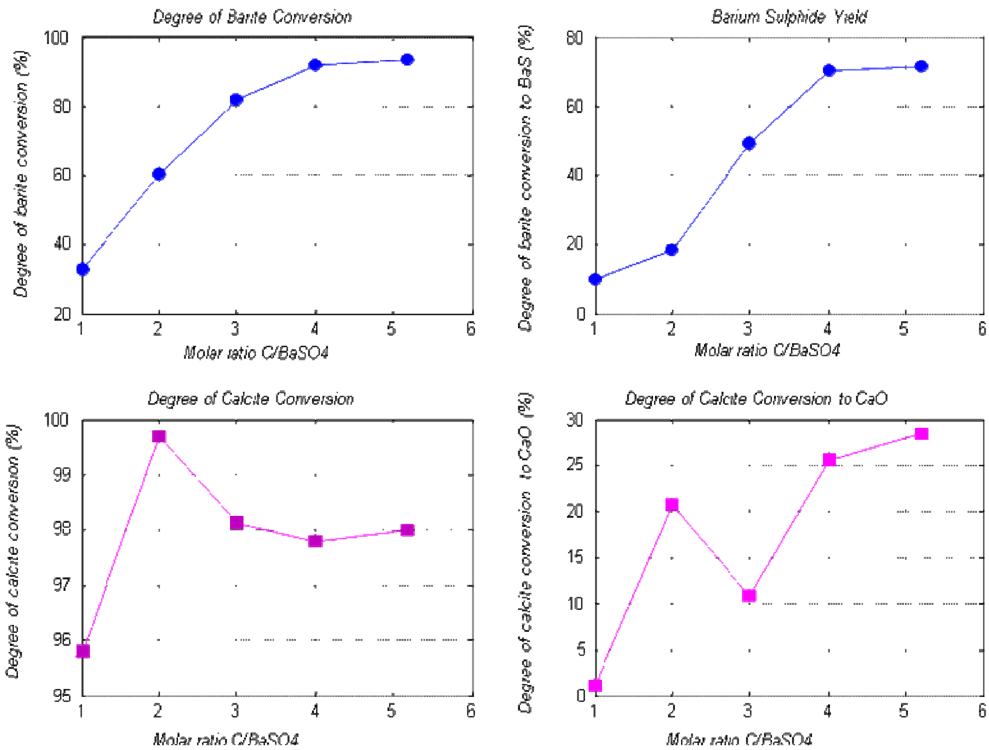
As given in Figure 8, both the barium sulphide yield and barite conversion gradually increases as the carbon/barite molar ratio increases, before they reach a plateau at a carbon/barite molar ratio of 4.0. The maximum barium sulphide yield and barite conversion as given in Figure 4 are approximately 70 % and 90 % respectively. The degree of calcite conversion reaches a maximum of 100 % at a carbon/barite molar ratio of 2.0 before reaching a plateau at 98 % at molar ratios of 3.0 and above. The conversion of calcite to calcium oxide generally increases with increase in carbon/barite molar ratio, with a maximum conversion not exceeding 30 %. However, as the carbon/barite molar ratio increases the degree of calcite conversion to lime and calcium sulphide gradually decreases to 20 % and 7.5 % respectively.

Reaction 1 shows the thermal conversion of barite to barium sulphide in the absence of oxygen. If oxygen is present under reducing conditions, carbon monoxide will form (Reaction 4) and acts as a reducing agent (Reaction 2).

$$2C\ (s) + O_2\ (g) \rightarrow 2CO\ (g) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

According to Alizadeh et al. (2007), carbon monoxide gas is formed when barite reacts with carbon at high temperatures. This then suggests that carbon monoxide is the major reducing agent during thermal processing of a barite/calcite sludge in the presence of carbon. The fact that maximum barium sulphide yield and barite conversion are observed at a carbon/barite molar ratio of 4.0 further supports the notion that carbon monoxide is the major reductant.

(**a**)



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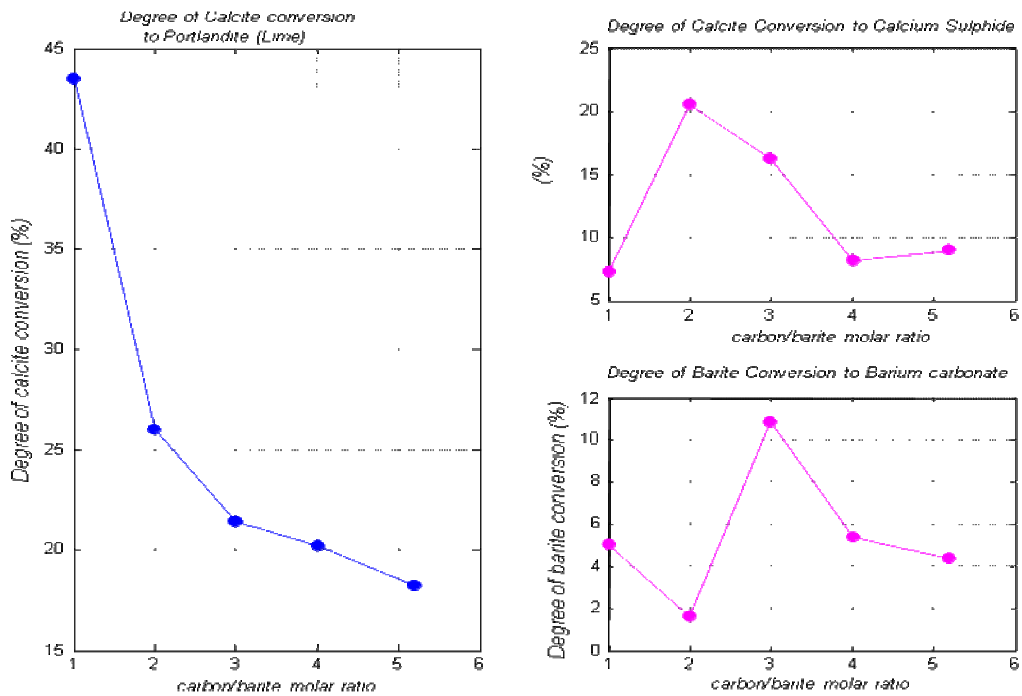

Figure 8. Effect of carbon/barite ratio; reaction time = 15 minutes; mass barite = 6.00 g (98% purity); mass calcite = 2.547 g (99% purity); temperature = 1030 °C

Overall, a 200 % dosage of coal (molar ratio carbon/$BaSO_4$ of 4.0) as opposed to stoichiometric quantities gives the best results. Based on this data, the carbon/barite molar ratio is the next most important parameter apart from temperature during thermal processing of a barite/calcite sludge.

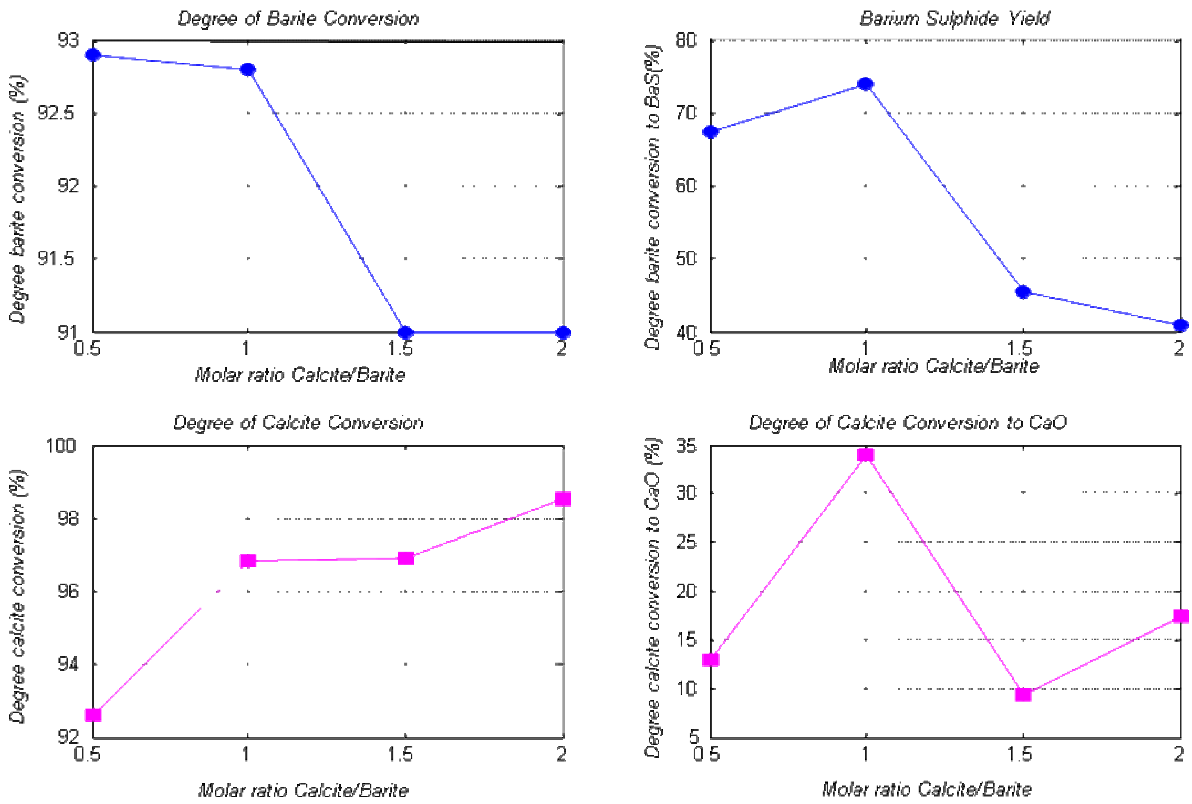

Figure 9. Effect of calcite/barite ratio

Based on Figure 9, maximum barium sulphide yield (75 %) and barite conversion (93 %) are reached at a calcite/barite molar ratio of 1.0. At calcite/barite molar ratios above 1.0, both the barium sulphide yield and degree of barite conversion decreases. This decrease is more significant for the barium sulphide yield where it drops from about 75 % to 45 % at a calcite/barite molar ratio of 1.5. The degree of calcite conversion ranges between 93-97 % when using calcite/barite molar ratios ranging from 0.5-2.0. In this regard, the degree of calcite conversion appears not to be affected significantly by the changes in the calcite/barite molar ratio.

Smaller particle sizes are known to increase the rate of the reaction due to the increased surface area which improves the chances of particle collision. In this regard, the effect of feed PSD was studied during the thermal process and results are given in Figure 10.

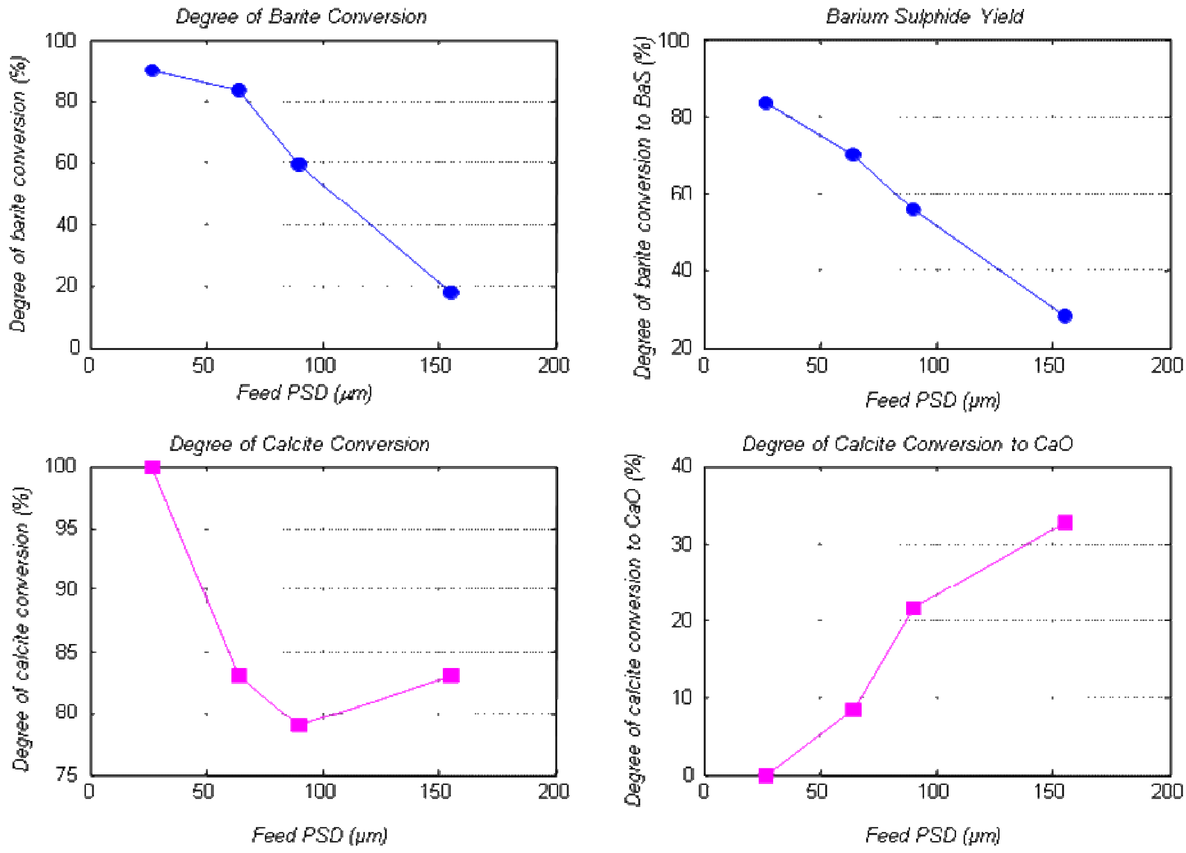

Figure 10. Effect of feed PSD

In Figure 10, the barium sulphide yield, degree of barite conversion and calcite conversion increased as feed PSD decreased. At a feed PSD of 0-50 μm, the degree of barite conversion of 90 % and barium sulphide yield of about 85 % are achieved. At higher feed PSD of above 100 μm the degree of barite conversion and barium sulphide yield are less than 20 % and 40 % respectively. The degree of calcite conversion is also high (~100 %) for feed PSD of 0-50 μm.

Overall, small feed particle size significantly increases the barite conversion and barium sulphide yield. In this regard, control of the precipitation reaction of BaSO4/CaCO3 to avoid the formation of crystals is important.

4.0 CONCLUSIONS AND RECOMMENDATIONS

Based on this study, gypsum sludge formation can be reduced by 80 % using the modified ABC, thereby maximizing generation of one type of sludge. Metals are completely removed during the lime neutralization, sulfidation and magnesium removal stages. The temperature is the driving force of the thermal reduction process, with the optimum temperature ranging between 1030-1100 ^{o} C. Apart from temperature, the carbon/barite molar ratio is also an important parameter, with 200 % coal dosage giving the best results at a temperature of 1030 ^{o}C using a reaction time of 15 minutes. A calcite/barite molar ratio of 1.0 gave the best results, while a small feed PSD ranging from 0-50 μm significantly increases the barite conversion and barium sulphide yield.

It is recommended that for future investigations pH controlled selective sulfide metal precipitation and XRD analysis of the precipitate be conducted in order to determine the amount of hydroxide and sulphide precipitation which will inform the sequence of operations during the neutralisation-precipitation process. These future investigations should also focus on the amount and composition of sludge generated vis-à-vis the traditional CSIR ABC process in order to evaluate the amount of barium carbonate required and the ease of separation during the sludge processing stage.

6.0 REFERENCES

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APPENDIX A. ESTIMATIONS OF THE CAPITAL AND RUNNING COST OF THE CSIR ABC PORCESS

AIM

The purpose of this investigation is to determine at a 50 % error margin the feasible of the CSIR ABC effluent treatment processes that is suitable for treatment of mine-water.

PROCESS DESCRIPTION

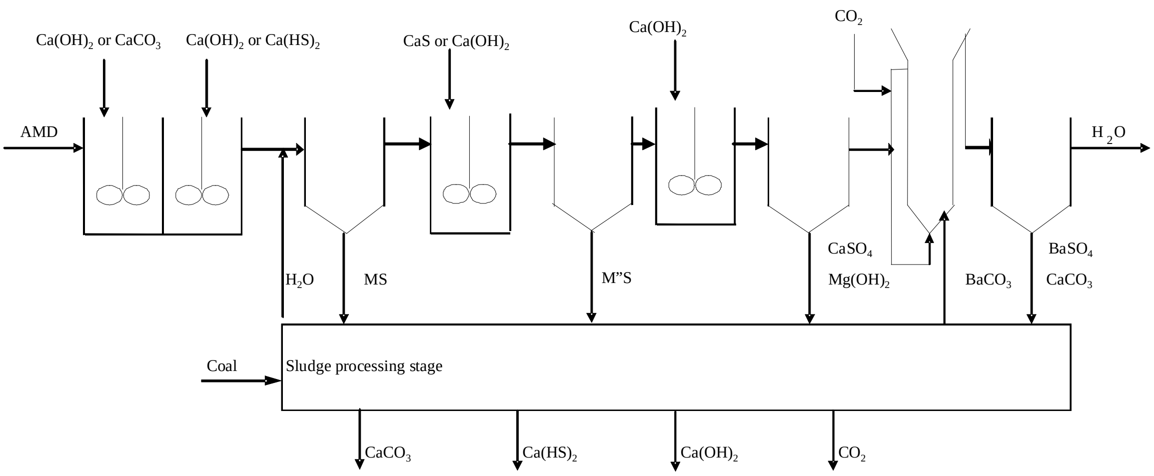
ABC (Alkali-Barium-Calcium) Desalination Process (CSIR)

Figure 1 shows the process flow-diagram of that part of the integrated process where the AMD is treated. The integrated process consists of the following chemical unit process stages, similar to those described previously:

- Limestone or lime neutralization of free acid.
- Sulphide precipitation of metals (FeII, FeIII and heavy metals) using calcium sulphide.
- Aluminium precipitation as $Al(OH)_3$.
- Magnesium precipitation as $Mg(OH)_2$ at high pH using lime.
- Separation of gypsum and metal-rich sludge from water.
- Leaching of metals from gypsum sludge.
- Recovery of CaS from gypsum.

Additional processes include the following:

- Sulphate removal through $BaSO_4$ using $BaCO_3$.



- Recovery of $BaCO_3$ from $BaSO_4$ using thermal treatment.

Figure 1. Process flow-diagram of the ABC process.

Either BaS or $BaCO_3$ can be used for sulphate removal (Maree *et al.*, 2004; Hlabela *et al.*, 2007). $BaCO_3$ was selected as it does not require subsequent H_2S stripping from the main water stream, but from a concentrated stream in the sludge processing stage. This novel process consists of the following stages:

- Pre-treatment using $CaCO_3$, or lime, for neutralization of the free acid and precipitation of iron(III) and aluminium(III), and CaS for precipitation of the heavy metals as sulphides.

$$H_2SO_4 + CaCO_3 \rightarrow CaSO_4 + CO_2 + H_2O \quad (1)$$

$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2H_2O \quad (2)$$

$$2M^{3+} + 3CaCO_3 + 3H_2O \rightarrow 2M(OH)_3 + 3CO_2 + 3Ca^{2+} \text{ (M = FeIII, Al)} \quad (3)$$

$$M^{2+} + H_2S \rightarrow MS + 2H^+ \text{ (M = FeII, Mn, Ni, Co)} \quad (4)$$

Lime treatment for magnesium removal and partial sulphate removal through gypsum crystallization,

$$Mg^{2+} + Ca(OH)_2 \rightarrow Mg(OH)_2 + Ca^{2+} \quad (5)$$

$$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow CaSO_4.2H_2O \quad (6)$$

An alternative is to use pure (external) lime to recover a clean magnesium hydroxide downstream of the barium stage.

- pH adjustment

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (7)$$

- Removal of sulphate as $BaSO_4$

$$Ca^{2+} + SO_4^{2-} + BaCO_3 \rightarrow BaSO_4(s) + CaCO_3(s) \quad (8)$$

- Processing of the $CaSO_4.2H_2O/Mg(OH)_2$ sludge to recover CaS and $CaCO_3$,

$$CaSO_4 + 2C \rightarrow CaS + 2CO_2 \quad (9)$$

- Processing of CaS to produce $Ca(HS)_2$, $CaCO_3$ and H_2S

$$2CaS + CO_2 + H_2O \rightarrow Ca(HS)_2 + CaCO_3 \quad (10)$$

$$Ca(HS)_2 + CO_2 + H_2O \rightarrow CaCO_3 + 2H_2S \quad (11)$$

- Processing of the $BaSO_4/CaCO_3$ sludge to recover BaS and CaO (dewatering and thermal processes) and finally,

$$BaSO_4 + 2C \rightarrow BaS + 2CO_2 \quad (12)$$

$CaCO_3 \rightarrow CaO + CO_2$ (13)

- Processing of BaS to produce $BaCO_3$

$BaS + CO_2 + H_2O \rightarrow BaCO_3 + H_2S$ (14)

- Processing of H_2S to sulphur, or alternatively to sulphuric acid.

$2H_2S + SO_2 \rightarrow 2S + 2H_2O$ (15)

$S + O_2 \rightarrow SO_2$ (17)

The water treatment section of the ABC Process has been evaluated on pilot scale (Photo 1). Table 2 shows the predicted water qualities after treatment in the various stages.

Table 2. Typical chemical composition of feed-water before and after the various treatment stages.

Parameter	Quality						
	Feed	**$CaCO_3$ neutra-lization**	**CaS dosage**	**Lime dosage**	**CO_2 dosage**	**$BaCO_3$ addition**	**SO_4 addition**
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 SO_4 values were adjusted to obtain ion balance.

Photo 1. Pilot-plant that was used for the evaluation of the CSIR ABC Desalination Process.

Procedure followed to determine the feasibility of the CSIR ABC process

The following approach was followed:

1. Chemical composition of feed and treated water after each stage. The various waters were electronically balanced by adjusting either the calcium or sulphate values.

2. Determine the following parameters for each process:
    a. Dosage, purity and utilization of main raw materials. The chemical dosage was calculated from the difference in water quality between two consecutive stages.
    b. Power consumption
    c. Yield and purity of products
    d. Delivered price of raw materials and sales price of products
    e. Estimated capital cost, capital redemption cost, maintenance, labor and power costs.

3. The chemical equations below were used to determine the following parameters:
    a. Chemical dosage of the raw materials
    b. Yield of products

Economic feasibility of the desalination processes

Table 3 shows the feasibility of the CSIR ABC process. Table 3 is in the form of a spreadsheet-based model which contains the following inputs and output for each of the processes:

Inputs:

- Chemical composition of feed and treated water for each of the treatment stages.
- Chemical dosage, calculated from the difference in chemical composition between feed-water and first treatment stage, or between two consecutive treatment stages. The chemical dosage makes provision for chemical purity and utilization efficiency.

Outputs:

- Product yield. This is calculated from the difference in chemical composition between feed-water and first treatment stage, or between two consecutive treatment stages. The product yield makes provision for chemical purity and product yield.
- Prices of raw materials and products.
- Estimated values for maintenance cost, labor cost, capital cost and capital redemption cost.
- Total running cost
- Total income
- Nett income

This approach was used for comparison of the various processes due to the following reasons:

- The cost of raw materials has the largest influence on the feasibility of a process.
- The values of figures for chemical dosage, chemical purity, chemical price and chemical yield can be adjusted for each application or market condition.
- Work load is minimized by expressing costs in terms of cost/m^3.

Table 3 shows that the feasibility of the ABC Process. The favorable cost can be explained by the following facts that count in its favor:

- Raw material needed for water treatment is produced on-site from sludges produced during water treatment. For example, lime is recovered from $CaCO_3$, $BaCO_3$ is recovered from $BaSO_4$, and CO_2 from coal. The only raw materials that need to be purchased are coal, $CaCO_3$ and $BaSO_4$ to supplement any losses.
- The input cost of the ABC process is low. This requires that products with low values need to be generated to have a feasible process. Processes that requires chemicals with a high cost, need to produce products with a high value. It is much more difficult for the latter processes to survive during periods when the economy is down, than for processes that use basic raw materials.

Table 3.a Chemical composition of feed and treated water and chemical dosages								
Parameter				Water quality and chemical dosage				
				Feed water	**$CaCO_3$**	**$Ca(OH)_2$**	**$BaCO_3$**	**CO_2**
Flow		(Ml/d)		25.00	25.00	25.00	25.00	25.00
Flow		m3/h		1042	1041.7	1041.7	1041.7	1041.7
Chemical dosage (Theor) (mg/l):					**938.9**	**1327.0**	**2,257.3**	**13.2**
Chemical dosage (Actual) (mg/l):					**1390.9**	**1734.7**	**2950.7**	**14.0**
Purity (%)					75	85	85	99
Equivalent mass					50	37	98.5	85.5
Utilization efficiency (%)					90	90	90	95
Salt rejection with HybridICE (%)								
Chemical consumption (t/d)					34.7737	43.3674	73.7677	0.351
Coal (70% C)		Coal	70			910.7	589.3	0.0
CO_2		CO_2						
Floc1								
Floc2								
Floc3								
Coal (70% C)		t/d coal				22.7679	14.7321	
Floc1		kg/d				0	0	0
Floc2		kg/d				0	0	0
Floc3		kg/d				0	0	0
Coagulant		kg/d						0.000

Chemical composition:						
pH		3.0	6.0	11.5	11.5	8.0
Free Alk						
Alkalinity	(mg/l as CaCO3)		0.0	900.0	50.0	170.0
Sulphate	(mg/l as SO4)	3,200	3,200.0	1,500.0	400.0	400.0
Chloride	(mg/l as Cl)		0.0	0.0	0.0	0.0
Fluoride			-	-	-	-
Sodium	(mg/l as Na)		0.0	0.0	0.0	0.0
Potassium	(mg/l K)		0.0	0.0	0.0	0.0
Magnesium	(mg/l as Mg)	205	205.0	0.0	0.0	0.0
Free acidity	(mg/l as CaCO3)	700.0	0.0	0.0	0.0	0.0
Iron(III)	(mg/l as Fe)		0.0	0.0	0.0	0.0
Aluminium	(mg/l as Al)	43	0.0	0.0	0.0	0.0
Manganese	(mg/l as Mn)	25	25.0	0.0	0.0	0.0
Iron(II)	(mg/l as Fe)		0.0	0.0	0.0	0.0
Cobalt	(mg/l as Co)		0.0	0.0	0.0	0.0
Nickel	(mg/l as Ni)		0.0	0.0	0.0	0.0
Copper	(mg/l Cu)	0.13	0.1	0.0	0.0	0.0
Zinc	(mg/l as Zn)	2.5	2.5	0.0	0.0	0.0
Selenium	(mg/l Se)		0.0	0.0	0.0	0.0
Strontium	(mg/l Sr)		0.0	0.0	0.0	0.0
Cadmium	(mg/l Cd)		0.0	0.0	0.0	0.0
Uranium	(mg/l U)		0.0	0.0	0.0	0.0
Silicon	(mg/l Si)		0.0	0.0	0.0	0.0
Barium	(mg/l Ba)		0.2	0.0	0.0	0.0
Lead	(mg/l Pb)		0.0	0.0	0.0	0.0
Calcium	(mg/l as Ca)	600.5	976.0	985.0	186.7	234.7
Ammonia	(mg/l as N)	0.0	0.0	0.0	0.0	0.0
TDS	(mg/l)	4,090.1	4,408.8	3,025.0	616.7	736.7
Total acidity	(mg/l as CaCO3)	938.9	0.0	0.0	0.0	0.0
Cations (+)		66.7	66.7	49.3	9.3	11.7
Anions (-)		66.7	66.7	49.3	9.3	11.7
Cations - Ca (+)		36.6	17.9	0.0	0.0	0.0
Anions - Alk						
Cations (+)		66.7	66.7	49.3	9.3	11.7

Table 3.b Sludge production								
Parameter			Water quality and chemical dosage					
						2.b		
				Feed water	CaCO3	Ca(OH)2	BaCO3	CO2
Sludge production:		**Concentration**						
Al(OH)3		mg/l			124.2	0.0	0.0	0.0
Fe(OH)3		mg/l			0.0	47.8	0.0	0.0
Mn(OH)2		mg/l			0.0	40.5	0.0	0.0
Zn(OH)2		mg/l			0.0	3.8	0.0	0.0
Co(OH)2		mg/l			0.0	0.0	0.0	0.0
Ni(OH)2		mg/l			0.0	0.0	0.0	0.0
Cu(OH)2		mg/l			0.0	0.2	0.0	0.0
U(OH)7		mg/l			0.0	0.0	0.0	0.0
SiO2		mg/l			0.0	0.0	0.0	0.0
CaSO4.2H2O		mg/l			0.0	7,310.0		
Mg(OH)2		mg/l			0.0	491.8	0.0	0.0
BaSO4		mg/l			0.0		2,669.8	0.0
CaCO3		mg/l			0.0		1,995.8	30.0
NH3		mg/l			0.0	0.0	0.0	0.0
Coal		mg/l				910.7	589.3	
Suspended solids		**mg/l**			**124**	**8,805**	**5,255**	**30**
Accumulated SS					**124**	**8,805**	**5,379**	**5,409**
		Load:						
Total Sludge (dry)		t/d			**3.1**	**220.1**	**131.4**	**0.8**
Total Acc Sludge (d		t/d			**3.1**	**220.1**	**134.5**	**135.2**
Total Acc Sludge (d		kg/h (dry)			**129**	**9,172**	**5,603**	**5,635**
Al(OH)3		t/d			3.11	0.00	0.00	0.00
Fe(OH)3		t/d			0.00	1.20	0.00	0.00
Mn(OH)2		t/d			0.00	1.01	0.00	0.00
Zn(OH)2		t/d			0.00	0.09	0.00	0.00
Co(OH)2		t/d			0.00	0.00	0.00	0.00
Ni(OH)2		t/d			0.00	0.00	0.00	0.00
Cu(OH)2		t/d			0.00	0.00	0.00	0.00
U2S7		t/d			0.00	0.00	0.00	0.00
SiO2		t/d			0.00	0.00	0.00	0.00
Gypsum		t/d			0.00	**182.75**	0.00	0.00
Mg(OH)2		t/d			0.00	**12.30**	0.00	0.00
BaSO4		t/d			0.00	0.00	66.74	0.00
CaCO3		t/d					49.90	0.75
Coal		t/d			0.0000	22.7679	14.7321	0.0000

Kiln products:								
Al2O3/Al2O3		t/d			3.0	0.0	0.0	0.0
Fe2O3		t/d			0.0	2.1	0.0	0.0
MnO		t/d			0.0	0.8	0.0	0.0
ZnO		t/d			0.0	0.1	0.0	0.0
CoO		t/d			0.0	0.0	0.0	0.0
NiO		t/d			0.0	0.0	0.0	0.0
Cu(OH)2/CuO		t/d			0.0	0.0	0.0	0.0
U2O7		t/d			0.0	0.0	0.0	0.0
SiO2/SiO2		t/d			0.0	0.0	0.0	0.0
CaS		t/d			0.0	76.5	**0.0**	0.0
MgO		t/d			0.0	8.5	0.0	0.0
BaO		t/d			0.0	0.0	59.7	0.0
CaO		t/d			0.0	0.0	37.8	0.6
Ash		t/d			0.0	6.8	4.4	0.0
Total		t/d				94.844	101.898	0.568
Total		kg/h				3951.834	4245.736	23.649
Sulphur production								
Sulphur		mg/l				1360	366.7	0.0
Sulphur		kg/h					381.9	0.0
Sulphur		t/d					9.2	0.0

Table 3.c Economic feasibility

Cost item	Tratment option				
	Feed water	**CaCO3**	**Ca(OH)2**	**BaCO3**	**CO2**
Flow (m3/h)	1,041.7	1,041.7	1,041.7	1,041.7	1,041.7
Chemical to repalce losses		CaCO3	Ca(OH)2	BaSO4	CO2
Mole ratio: Replacement/Used chemical		1.00	1.00	1.18	1.00
Chemical dosage (actual) (mg/l)		1391	1735	3490	14
Price (R/t)		220	1,300.0	2000	0
Losses to replace (%)		100	100.0	6	0.0
Chemical cost (R/m3)		0.31	2.26	0.42	-
Coal usage (mg/l)			911	589	0
Coal price (R/t)			300	300	
Coal cost (R/m3)			0.27	0.18	-
Other chemical cost (e.g. flocculants) (R/m3)		0.03	0.03	0.03	0.03
Energy consumption (kWh/m3)		1.00	1.00	1.00	1.00
Energy cost (R/kWh)		0.30	0.30	0.30	0.30
Energy Cost (R/m3)		0.30	0.30	0.30	0.30
Labour cost (R/m3)		0.20	0.30	0.40	0.20
Maintenance cost (R/m3)		0.20	0.30	0.40	0.20
Admin cost (/m3)		0.05	0.08	0.10	0.05
Running Cost (R/m3)		**1.09**	**3.53**	**1.83**	**0.78**
Total Running Cost (R/m3)		**7.22**			
Products					
Water					
Zn(OH)2 (mg/l)		0.0	3.8		
Sulphur (mg/l)			1,360	367	
Ca(OH)2 (mg/l)			3,145	1,477	22
(NH4)2SO4 (mg/l)					
MgSO4 (mg/l)					
Mg(OH)2 (mg/l)					
Recovery (%)		90	80	80	80
Production:					
Water (tm3/h) (80% recovery)		833.3	833.3	833.3	833.3
Zn(OH)2 (t/d)		-	0.08		
Sulphur (t/d)			27.20	7.33	-
Ca(OH)2 (t/d)			62.90	29.54	0.44
(NH4)2SO4 (t/d)			-	-	-
MgSO4 (t/d)			-	-	-
Mg(OH)2 (t/d)			-	-	-

Price:					
Water (R/t)			1.50	3.00	3.00
Zn(OH)2 (R/t)		3000	3,000.0		
Sulphur (R/t)		800	800.0	800.0	800.0
CaCO3 (R/t)		1000	1,000.0	1,000.0	1,000.0
(NH4)2SO4 (R/t)		1200	1,200.0	1,200.0	1,200.0
MgSO4 (R/t)		1100	1,100.0	1,100.0	1,100.0
Mg(OH)2 (R/t)		1500	1,500.0	1,500.0	1,500.0
Value					
Water (R/m3)		-	-	-	3.00
Zn(OH)2 (R/m3)		-	0.01		
Sulphur (R/m3)		-	0.87	0.23	-
Ca(OH)2 (R/m3)		-	2.52	1.18	0.02
(NH4)2SO4 (R/m3)		-	-	-	-
MgSO4 (R/m3)		-	-	-	-
Mg(OH)2 (R/m3)		-	-	-	-
Value (R/m3)		**-**	**3.40**	**1.42**	**3.02**
Total value (R/m3)		**7.83**			

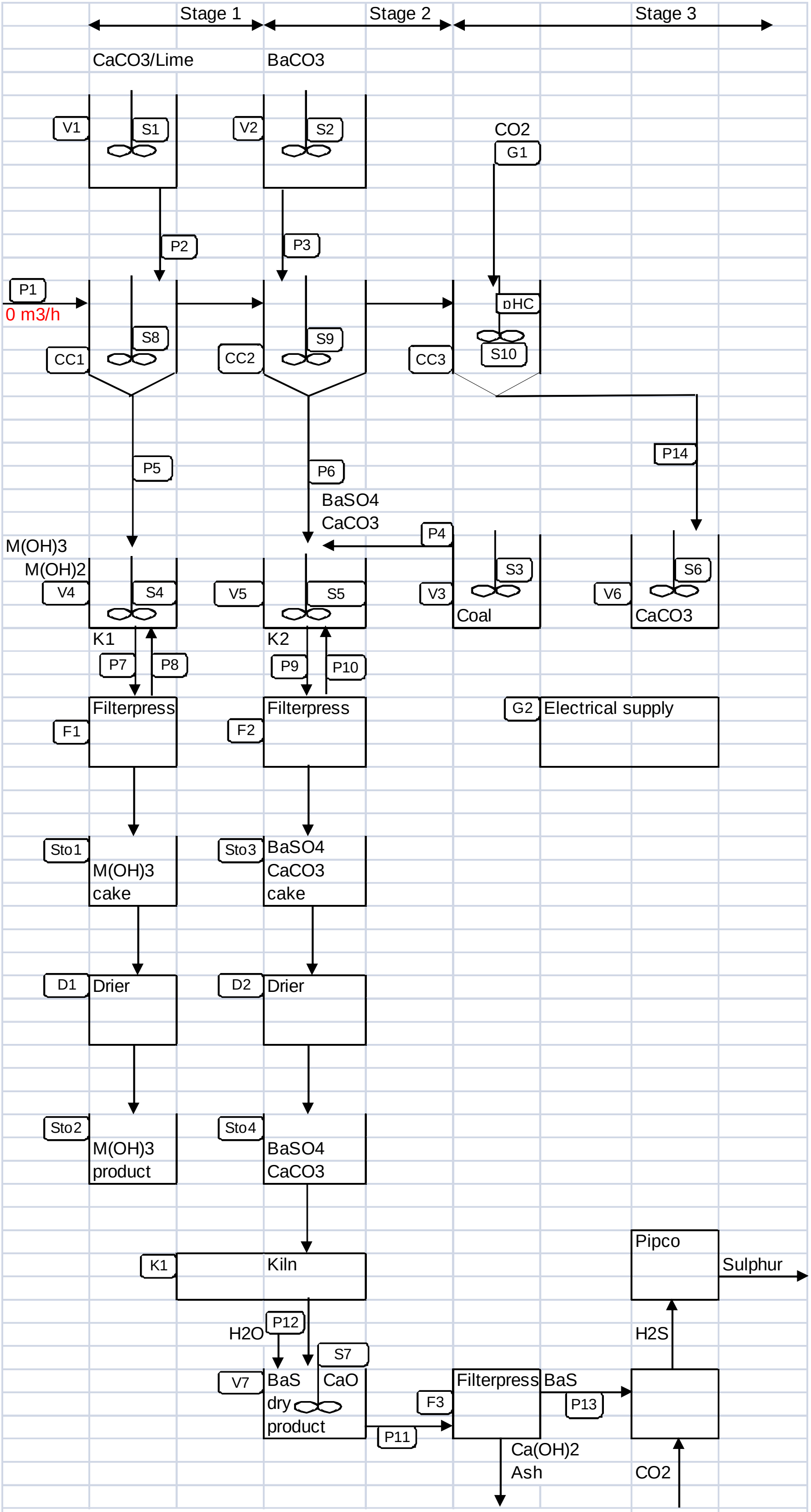


Figure 1. PFD of Integrated process for with the CSIR ABC process

Table 3.d Equipment list and capital cost

Item No	Reactor	Flow	HRT	Volume	Area	Dia	Height	Upflow vel	Concentration	pH	Cost
		m3/h	h	m3	m2	m	m	m/h	%		R
	Capital cost (R)										**137,021,068**
	Capital cost (R/Ml/d)										**5,480,843**
	Equipment (R)										**66,839,545**
V1	Alkali storage	32.56	48	1563		12.58	12.58				149,458
V2	Ba alkali storage	30.74	48	1475		12.34	12.34				141,908
V3	Coal storage	15.63	48	750		9.85	9.85				77,189
V4	M(OH)3 slurry	0.86	6	5		1.87	1.87				876
V5	BaSO4 slurry	36.49	6	219		6.53	6.53				25,487
V6	CaCO3 slurry	0.08	6	0.5		0.84	0.84				101
V7	Kiln product slaking	27.81	1	28		3.28	3.28				3,979
CC1	M(OH)3 reactor/clarifier - reactor	1042	0.5	521	37.62	6.92	13.84	83.06			55,594
CC1	M(OH)3 reactor/clarifier - clarifier	1042	3.2	3352	520.83	27.40	15.84	2			3,860,870
CC2	BaSO4 reactor/clarifier - reactor	1042	1.0	1042	59.73	8.72	17.44	52.32			414,969
CC2	BaSO4 reactor/clarifier - clarifier	1042	2.9	3028	520.83	27.91	19.44	2			3,523,477
CC3	CaCO3 reactor/clarifier - reactor	1042	0.5	521	37.62	6.92	13.84	83.06			222,376
CC3	CaCO3 reactor/clarifier - clarifier	1042	3.2	3352	520.83	27.40	15.84	2			3,860,870
S1	Alkali stirrer	32.56	48.00	1562.82		12.58	12.58				74,729
S2	Ba alkali stirrer	30.74	48.00	1475.35		12.34	12.34				70,954
S3	Coal stirrer	15.63	48.00	750.00		9.85	9.85				38,594
S4	M(OH)3 slurry stirrer	0.86	6.00	5.18		1.87	1.87				438
S5	BaSO4 slurry stirrer	36.49	6.00	218.95		6.53	6.53				12,743
S6	CaCO3 slurry stirrer	0.08	6.00	0.47		0.84	0.84				50
S7	BaO slaking stirrer	27.81	1.00	27.81		3.28	3.28				1,990
S8	M(OH)3 reactor/clarifier - reactor	1042	0.5	521	38	6.92	14	83			27,797
S9	BaSO4 reactor/clarifier - reactor	1042	1.0	1042	60	8.72	17	52			51,871
S10	BaSO4 reactor/clarifier - clarifier	1042	0.5	521	38	6.92	14	83			27,797
P1	Feed water pump	1042								2.7	622,454
P2	Alkali dosing dosing	32.56							10	10	117,118
P3	Ba dosing	30.74							10	12.5	111,202
P4	Coal dosing	15.63							10	5	60,487
P5	M(OH)3 sludge withdrawal	0.86							15	9	4,461
GypSLiM	Gypsum/Mg(OH)2 sludge withdrawal	61.14							15		206,513
P6	BaSO4 sludge withdrawal	36.49							15	11.5	129,780
P7	M(OH)3 slurry to filter press	0.86							15	9	4,461
GypSLiM	Gypsum/Mg(OH)2 slurry to filter press	61.14									206,513
P8	M(OH)3 filter press return water	0.68								9	3,591
P9	BaSO4 slurry to filter press	36.49							15	11.5	129,780
P10	BaSO4 filter press return water	28.67								11.5	104,459
GypSLiM	CaS/MgO slurry to filter press	35.42							10		126,331
GypSLiM	CaS solution to H2S stripper	35.42							10		126,331
P11	BaO/MgO slurry to filter press	27.81							10	12.5	101,627
P12	Water to kiln product	27.81									101,627
P13	Ba alkali solution to V2	27.81								11.5	101,627
P14	CaCO3 sludge withdrawal	0.08							40	8.5	514
F1	Filter press 1 M(OH)3	0.86									173,446
F2	Filter press 2 (BaSO4/MgOH)2)	36.49									5,045,365
F3	Filter press 3 (Ba alkali/ash separation)	27.81									3,950,895
GypSLiM	Filter press CaCO3										
Sto1	M(OH)3 cake storage	48		170.36					70		20,335
Sto2	M(OH)3 dried product storage	48		149.07					100		18,032
Sto3	BaSO4 cake storage	48		4003.74					70		348,513
Sto4	Dried BaSO4/Mg(OH)2 storage	48		4003.74					100		348,513
D1	M(OH)3 cake drier										47,326
D2	Kiln feed cake drier										1,376,677
K1	Kiln										33,040,251
	Iron(II)-oxidation and sulphur separation	1042									7,507,197
pHC	pH Control										30,000
G1	CO2 dosing										30,000
G2	Electrical supply (20%)										13,367,909
	Piping (10%)										6,683,955
	Valves and Instrumentation 5%)										3,341,977
	Design and Engineering (20%)										13,367,909
	Construction (50%)										33,419,773