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Phosphogypsum Conversion to Calcium Carbonate and Utilization for Remediation of Acid Mine Drainage

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Abstract

The conversion of phosphogypsum waste (a waste product of phosphoric acid production in Richard Bay, South Africa), using sodium carbonate was tested. Response surface methodology (RSM) was used to investigate the combined effect of relevant process variables to maximize the production of calcium carbonate in a batch reactor. The process variables include time (0, 60, and 120 min); slurry content (5, 10, and 15%); agitation speed (100, 300, and 500 rpm); and sodium carbonate/gypsum molar ratio (0.8, 1.4, and 2). In the optimum conditions of the process (the slurry concentration of 5%, molar ratio sodium carbonate/gypsum of 2, stirring rate of 500 rpm) the conversion of waste gypsum to calcium carbonate after 105 minutes reaches over 98.5%. The calcium carbonate produced in this work compares favorably to the commercial calcium carbonate (laboratory grade) during Acid Mine Drainage (AMD) neutralisation.

Keywords: Optimization; Waste gypsum; Calcium carbonate; Acid Mine Drainage

Introduction

South Africa has a highly-developed domestic and export oriented phosphate industry with the largest igneous phosphate deposit located in Phalaborwa in the low veld of the Northern Province of the country. Waste gypsum is produced as a by-product during treatment of phosphate concentrate with sulphuric acid to produce phosphoric acid according to the following simplified reaction:

$$Ca10(PO4)6F2 + 10H2SO4 + 20H2O = 10CaSO4.2H2O + 6H3PO4 + 2HF \quad (1)$$

The Richard Bay Foskor phosphoric acid plant is a complex import/export orientated industry with raw materials including large quantities of phosphate rock from Phalaborwa and approximately 350 000 tonnes of sulphur which are imported annually. The bulk of the phosphoric acid produced in Richard Bay is exported whilst approximately 10% is used in South Africa for the manufacture of phosphatic fertilizers and animal feeds. The effluent from this plant consists of about 10 000 tonnes/day of waste gypsum, containing 20-30% free water and which is pumped into the sea or stockpiled. The readily apparent disadvantages of these disposal options is that it results in loss of all commercial value or poses environmental threat by the leaching action of rainwater and/or storage water producing an acidic effluent that may enter the nearby surface and/or groundwater regime, creating an environmental hazard [1].

The beneficiation of the waste gypsum generated during production of phosphoric acid has been for a long time an important challenge for the phosphoric acid industry, ecologists and all those concerned with disposal of waste products such as government and civil society. In view of the chemical characteristics of waste gypsum from the phosphoric acid industry (more than 93% is CaSO4.2H2O) and its economic potential, and of the prevailing environmental pollution concerns there is a clear value in promoting the use of waste gypsum as an alternative raw material for many applications. Hitherto a number of options for waste gypsum beneficiation have been proposed in South Africa:

Fertilizer and soil conditioner

Around 40.000 tonnes per year of waste gypsum are sold by the Omnia group to the agriculture sector. Waste gypsum has been also used worldwide as an agricultural fertiliser or for soil stabilisation amendments [2,3].

Cement and wallboard

The Omnia group upgrades around 200.000 tonnes per year of waste gypsum for use in the cement industry. The use of waste gypsum has been also elsewhere reported in the cement industry as a setting regulator in place of natural gypsum [4].

Road construction materials

Unfortunately, these solutions have not proven reliable in terms of large-scale volume reduction of waste gypsum.

Security of water supply has become a key strategic issue for the sustained economic growth of South Africa as it is a water-stressed country. Although the South African mining sector is one of the critical pillars and drivers of the South African economy, mining activities are also associated with environmental pollution such as acid mine drainage (AMD). AMD is highly acidic water, usually containing high concentrations of metals, sulphides, and salts as a consequence of mining activity. The major sources of AMD include drainage from underground mine shafts, runoff and discharge from open pits and mine waste dumps, tailings and ore stockpiles, which make up nearly 88% of all waste produced in South Africa. The gold mining industry in South Africa (principally the Witwatersrand Goldfield) is in decline, but the post-closure decant of AMD represents an enormous threat. For example, the potential volume of AMD for the Witwatersrand

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Goldfield alone amounts to an estimated 350ML/day [5-8]. While some mines have established ad hoc treatment processes to treat localized water pollution, South Africa urgently needs a regional, consolidated approach to AMD. It is against this background that the government of South Africa has suggested that the pumping and partial treatment of mine water is critical and should be implemented in the short term in the western, central and eastern basins through neutralisation and metals removal. The partial treatment of mine water to neutralise acidity and remove metals will require considerable amount of calcium carbonate which will put extra pressure on the existing local market. It is therefore imperative that alternatives options of calcium carbonate production be considered. In this paper we consider the use of sodium carbonate for waste gypsum treatment and recovery of calcium carbonate. We have completed batch laboratory tests required to gather process data and determine the best process conditions for optimized production of calcium carbonate from waste gypsum using sodium carbonate. Response Surface Methodology (RSM) was used to optimize the waste gypsum conversion.

Materials and Methods

Feed stock material

Identification of mineralogical characteristics of phosphogypsum waste is important from processing viewpoint as the beneficiation of waste gypsum is in some extent controlled by mineralogical and textural characteristics. Samples of phosphogypsum from the Foskor plant in Richards Bay (South Africa) were collected for this study. Splits of these samples were subjected to chemical and physical analyses. The data on particle size distribution were obtained by MICROTRAC S3500 Particle Size Analyser. The waste gypsum used in this work has a particle size ranging between 0.003 and 0.055 mm in diameter with an average particle size of 0.017 mm in diameter. X-Ray Fluorescence (XRF) Oxford Instruments TWIN-X and HITACHI S-7000 Scanning Electron Microscope (SEM) were used to determine the elemental composition and morphological structure of the waste gypsum. X-Ray Fluorescence (XRF) results in Table 1 show the collected phosphogypsum generally contains traces of Co, Cu, Zn, Ga, Sr, Y, Zr, Ba, Ce, W, Pb and Th and some rare earth elements like Y. The morphological structure of untreated phosphogypsum samples, as determined by SEM, is illustrated in Figure 1 and reveals a homogeneous, prismatic piling arrangement. Radioactivity analysis was also conducted on the Foskor phosphogypsum for gross alpha/beta-activity and for selected radio nuclides in the uranium and thorium decay series by the South African Nuclear Energy Corporation and the result shows that the collected phosphogypsum contains low levels of U-series radionuclide. The most important source of radioactivity is 226Ra and 228Ra as shown in Table 2. Other researchers have reported a wide variety of radionuclide concentrations in different phosphogypsum sources [9,10]. The concentrations of Ra-226 and Ra-228 are respectively 316 and 424 Bq/kg in Foskor phosphogypsum.

Equipment

Waste Gypsum treatment experiments were carried out batch-wise using a 3 litre Perspex reactor as shown in the experimental setup (Figure 2). The reactor had four equally spaced baffles and was equipped with an outer flow jacket. An overhead stirrer equipped with a radial turbine impeller was used for mixing combined with an external recirculation pump. A Hanna HI2829 multi-parameter meter was used to log electrical conductivity, pH and temperature data. A hypodermic syringe was used to draw out sample aliquots from the gypsum reactor. A PERKIN ELMER ANALYST 700 Atomic Absorption Spectrometer (AAS) and a VARIAN Inductively Coupled Plasma (ICP) spectrometry were used to analyse for Ca and Na during experiments. A LECO CS200 carbon/sulphur analyser was used to determine the inorganic Carbon (C) content of the calcium carbonate produced.

Experimental procedure

Waste gypsum treatment experiments was carried out by mixing

Cr (%)	Mn (%)	Fe (%)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Ga (ppm)	Ge (ppm)	As (ppm)	Se (ppm)
0.025	0.01	0.07	51.90	12.40	12.90	22.31	7.81	<1.20	0.71	1.31
Br(ppm)	**Rb(ppm)**	**Sr(ppm)**	**Y(ppm)**	**Zr(ppm)**	**Ag(ppm)**	**Cd(ppm)**	**Sn(ppm)**	**Sb(ppm)**	**Te(ppm)**	**I(ppm)**
3.100	2.60	2183	105.61	11.11	<0.71	1.71	<0.91	1.30	0.51	<2.51
Cs(ppm)	**Ba(ppm)**	**La(ppm)**	**Ce(ppm)**	**Hf(ppm)**	**Ta(ppm)**	**W(ppm)**	**Tl(ppm)**	**Pb(ppm)**	**Th(ppm)**	**U(ppm)**
<5.1	216.90	594.30	1435	11.71	10.90	34.00	2.40	18.90	20.21	4.41
Al (%)	**Na (%)**	**Mg (%)**	**Si (%)**	**P (%)**	**S (%)**	**K (%)**	**Ca (%)**	**Ti (%)**	**V (%)**	
<0.018	<0.45	<0.08	0.34	0.80	19.66	<0.01	25.52	<0.01	0.02	

Table 1: Chemical composition (wt. %) of the Foskor phosphogypsum as determined by XRF analysis.

Phosphogypsum raw material				Calcium carbonate produced			
Nuclide	**Value(Bq/kg)**	**Unc.**	**MDA**	**Nuclide**	**Value (Bq/kg)**	**Unc.**	**MDA**
^{238}U	14.71	0.51	0.59	^{238}U	8.65	0.43	0.60
^{234}U	14.81	0.51	0.60	^{234}U	8.72	0.43	0.61
^{226}Ra	316	32	90	^{226}Ra	413	37	99
^{210}Pb	171	20	48	^{210}Pb	237	24	51
^{235}U	0.68	0.03	0.03	^{235}U	0.40	0.02	0.03
^{228}Ra	424	18	33	^{228}Ra	442	20	42
^{228}Th	114	6	8.81	^{228}Th	123	6	11
^{40}K	< MDA	-----	140	^{40}K	< MDA		160

Table 2: Analysis of Foskor phosphogypsum and produced calcium carbonate for selected radionuclide (Bq/kg).

The uncertainty (Unc. column) is quoted at 1 sigma (or coverage factor k = 1). The uncertainty is calculated mainly from counting statistics and it is not the standard deviation obtained from replicate measurements. No uncertainty value is reported of a less than MDA ("< MDA") is indicated in the Value column. The minimum detectable activity concentration (MDA column) is calculated with a 95% confidence level.

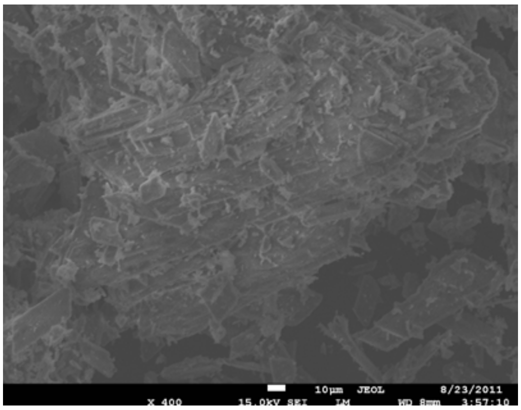

Figure 1: SEM micrograph of the Foskor phosphogypsum.

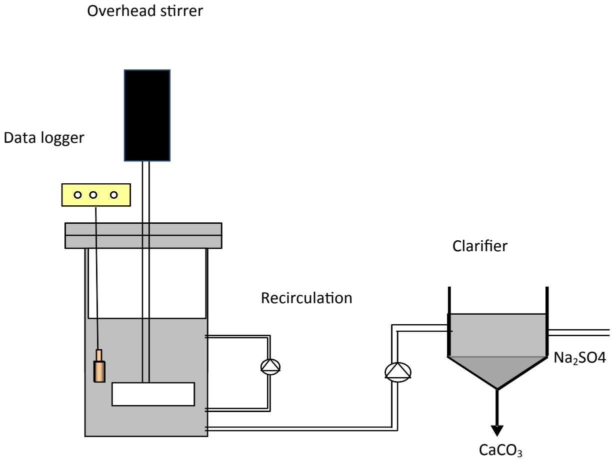

Figure 2: Experimental Setup.

100 g of waste gypsum with a pre-calculated amount of water and placed in the reactor. The slurry was then mixed for 20 minutes for ambient experiments or heated up to a predetermined temperature under continuous agitation for experiments above ambient temperatures until stabilization. A certain amount of sodium carbonate corresponding to different molar ratios was introduced into the reactorand reacted for defined time period. Sample aliquots were collected at predetermined time intervals over the entire reaction period. The collected samples were immediately filtered; the sulphate content determined by standard analytical procedures as described in Standard Methods for the Examination of Water and Wastewater (APHA, 1985). The calculation of the reaction conversion applied to all the experimental data is as follows:

Reaction conversion (%) = (Sulphate in filtrate /sulphate in feed sample) × 100 (2)

Results and Discussion

Statistical analysis

Optimization of process conditions is usually one of the most important factors to reduce the production cost. The conventional method, which involved varying one variable at a time while keeping the other variables constant is lengthy and often does not produce the effect of interaction of different variables. To this end, Response Surface Methodology (RSM) was used to optimize the waste gypsum conversion. Laboratory scale confirmation of the products was then used to validate the feasibility of the derived optimum conditions. The tests were performed to investigate mainly the effect of the investigated factors on the waste gypsum conversion to calcium carbonate. Four factors were taken into consideration in the experimental planning: time (min) (A); slurry content (%) (B); Molar ratio of sodium carbonate to gypsum (C) and stirring speed (rpm) (D) as shown in Table 3.

The efficiency of fit of the model was checked by the determination coefficient (R2). In this case, the value of the determination coefficient (R2 = 0.96) indicates that only 4% of the total variations are not explained by the model (Table 5). The R2 value for phosphogypsum conversion indicates that the proposed model is adequate with no significant lack of fit as 96 % of the variability in the response could be explained by the model. The value of the adjusted determination coefficient (Adj. R2 = 0.91) is also very high, which indicates a high significance of the model. R2 values increase as more variables are

Variable	Parameter	Low Value	Median Value	High Value
Time (min)	A	0	60	120
Slurry (%)	B	5	10	15
Molar ratio (Na_2CO_3/ Gypsum)	C	0.8	1.4	2
Stirring speed (rpm)	D	100	300	500

Table 3: Levels of factors chosen for the experimental design.

Experiment No.	t (min), A 30,45, 60	Slurry (%), B 5, 10, 15	Molar ratio, C (moles Na_2CO_3/ moles gypsum) 0.8, 1.4, 2	v(rpm) D 100, 300; 500	Phospho-gypsum Conversion (%)
1	0	5	0.80	100	7
2	120	5	0.80	100	54
3	0	15	0.80	100	2.61
4	120	15	0.80	100	52
5	0	5	2	100	12.60
6	120	5	2	100	86
7	0	15	2	100	2.40
8	120	15	2	100	37
9	0	5	0.80	500	11
10	120	5	0.80	500	72
11	0	15	0.80	500	4.43
12	120	15	0.80	500	58
13	0	5	2	500	4.8
14	120	5	2	500	97
15	0	15	2	500	5.60
16	120	15	2	500	61.71
17	0	10	1.40	300	4.32
18	120	10	1.40	300	58.81
19	60	5	1.40	300	69
20	60	15	1.40	300	51
21	60	10	0.80	300	53
22	60	10	2	300	62
23	60	10	1.40	100	42
24	60	10	1.40	500	83
25	60	10	1.40	300	58.21
26	60	10	1.40	300	57.91
27	60	10	1.40	300	59.61

Table 4: Experimental results for treatment of Foskor phosphogypsum with Sodium Carbonate using central composite design.

added to a model; the adjusted R2 is often used to summarize the fit as it takes into account the number of variables in the model. For multiple regression, although R2 is still the percent of the total variation that can be explained by the regression equation, the largest value of R2 will always occur when all of the predictor variables are included, even if those predictor variables don't significantly contribute to the model. R2 will only decrease or stay the same as variables are removed, but never increase. The Adjusted R2 uses the variances instead of the variations. That means that it takes into consideration the sample size and the number of predictor variables. The value of the adjusted R2 can actually increase with fewer variables or smaller sample sizes.

This correlation is also proven by the plot of predicted versus experimental values of phosphogypsum conversion in Figure 3. Other elements, such as Ca and Na, were not considered as response factors because the only important parameter for following the reaction process evolution was considered to be the sulphate removal. However for the purpose of this study the solubilization of Ca was also monitored and was always very low (0.1-0.5 mg/1). In Table 5 the coefficients A, B, D and A2 are all significant model terms.

The effect of the independent variables, slurry (%) and time on the phosphogypsum conversion can be accessed from Table 4. Phosphogypsum conversion mainly depend on the reaction time since both its linear and quadratic effects are significant (Prob>|t| less than 0.05). The waste gypsum conversion is decreased when the phosphogypsum slurry content (%) is increased. Table 4 shows that the linear effect of the slurry content has a negative sign. However the quadratic effect of the slurry content on the phosphogypsum conversion has a positive sign, which suggests that the phosphogypsum conversion will have a curvilinear shape in the time-slurry (%) space as the negative value of the linear slurry coefficient will cause an initial downward slope, and the positive value of the coefficient for the slurry quadratic terms will cause the curve linearity (upward due to the positive sign). The effect of the independent variables, time and sodium carbonate/gypsum molar ratio on the waste gypsum conversion can also be assessed from Table 4. The phosphogypsum conversion does not depend significantly on the sodium carbonate/gypsum molar ratio as both its linear and quadratic effects are not significant (Prob>|t| more than 0.05). However the phosphogypsum conversion to calcium carbonate depends on the stirring speed as its linear effect is significant.

Term		Estimate	Std Error	t Ratio	Prob>|t|
Intercept		58.34	3.51	16.60	<.0001*
Time (min)(0,120)	A	29.30	2.09	14.03	<.0001*
slurry (%)(5,15)	B	-7.45	2.09	-3.57	0.0044*
Molar Ratio(0.8,2)	C	3.10	2.09	1.49	0.1654
Stirring Rate (rpm)(100,500)	D	5.59	2.09	2.67	0.0217*
Time (min)*slurry (%)	AB	-4.80	2.22	-2.16	0.0533
Time (min)*Molar Ratio	AC	2.92	2.22	1.32	0.2143
slurry (%)*Molar Ratio	BC	-4.21	2.22	-1.90	0.0841
Time (min)*Stirring Rate (rpm)	AD	3.73	2.22	1.68	0.1205
slurry (%)*Stirring Rate (rpm)	BD	0.61	2.22	0.27	0.7888
Molar Ratio*Stirring Rate (rpm)	CD	-0.08	2.22	-0.04	0.9707
Time (min)*Time (min)	A^2	-26.45	5.54	-4.78	0.0006*
Slurry (%)*slurry (%)	B^2	1.65	5.54	0.30	0.7714
Molar Ratio*Molar Ratio	C^2	-0.85	5.54	-0.15	0.8807
Stirring Rate (rpm)*Stirring Rate (rpm)	D^2	3.15	5.54	0.57	0.5811

*significant

Table 5: Analysis of the response surface quadratic model obtained from experimental designs.Prob>|t| less than 0.05 indicate model terms that are significant, R^2 = 0.961226, Adjusted R^2 = 0.911878, t Ratio are equal to the coefficients/std errors.

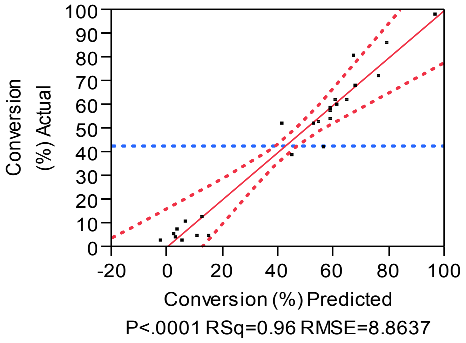

Figure 3: Actual (experimental) response conversion (%) versus predicted (model) conversion (%).

There are a number of combinations of variables that could give maximum levels of phosphogypsum conversion. The optimum experimental conditions were obtained by the differentiation of the quadratic model using an algorithm carried out on the Maple 9.5 program (Waterloo Maple, Inc., Canada) to achieve maximum phosphogypsum production. The derived optimum conditions were: Time = 105 min, phosphogypsum slurry concentration = 5%, sodium carbonate/phosphogypsum molar ratio = 2 and speeding rate = 500 rpm. The predicted waste gypsum conversion corresponding to these levels was 98.6%.Validation of the predicted results was accomplished by performing additional experiments in duplicate with the parameters suggested by the numerical modeling. The two experiments yielded an average waste gypsum conversion of 98.4%. Good agreement between the predicted and experimental results confirmed the experimental adequacy of the model and the existence of the optimal conditions.

Application

The quality and the neutralisation potential of the precipitated calcium carbonate produced by conversion of waste gypsum using sodium carbonate were assessed. Partial treatment, as normally applied to Acid Mine Drainage, involves chemical neutralization of the acidity followed by precipitation of iron and other suspended solids and usually the chemicals used for Acid Mine Drainage treatment include limestone and hydrated lime [11-14]. The use of limestone requires that its calcium content be as high as possible to reduce the drawbacks for using limestone which include slow reaction time. In the case of limestone, the neutralization process can be described as the replacement of the undesirable cation components (H+, Fe2+, Fe3+) in AMD by a more acceptable cation, which is Ca2+ and the overall reaction can be written as follows:

CaCO3(s) + 2H+ = Ca2+ + H2O + CO2

XRF analyses were conducted to identify elemental composition of the calcium carbonate produced at the optimum conditions derived above.

The main objective of the product evaluation was to compare the

Parameter	pH	Acidity	SO_4^{2-}	Ca	Cl^-	Fe	Mg	Mn	Na	Al
Units		mg $CaCO_3$	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Values	3.01	125	2700	468	45	246	135	70	82	2.62

Table 6: Typical composition of Acid Mine Drainage neutralized using calcium carbonate.

Sample	Inorganic C	SiO_2	SO_4^{2-}	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	Cr_2O_3
Commercial $CaCO_3$	54.31	0.49	0.07	0.26	0.07	0.19	58.13	< 0.16	< 0.01	0.04
Produced $CaCO_3$	48.93	1.63	2.41	0.36	0.01	< 0.05	46.84	2.49	0.01	0.04

Table 7: Produced and commercial composition (wt. %) for major oxides, inorganic carbon as determined by XRF and LECO analysis.

neutralizing potential of the produced calcium carbonate vis-à-vis the commercial calcium carbonate. The test consists of simple stirred beaker filled with 100 ml AMD of composition shown in Table 6 and 200 mg of the neutralizing material (calcium carbonate). The pH was followed through the entire testing period.

The main results of the batch tests performed with the two types of calcium carbonate are presented in Table 7. This test allows evaluating the influence of the composition of the limestone. There is a rapid increase of pH during the first 2 minutes from 3.2 to 5.6 for commercial calcium carbonate and to 4.5 for calcium carbonate produced by treatment of phosphogypsum with sodium carbonate. Then a difference in the neutralization potential between these two calcium carbonates is monitored. However both solutions reach a pH of 6.9 after 60 minutes Figure 4. These results confirm that the neutralizing potential of the produced calcium carbonate is comparable in the long run to that of commercial calcium carbonate although the calcium and inorganic carbon content of the produced calcium carbonate is slightly lower than that of commercial calcium carbonate as shown in Table 7. The radionuclide in the calcium carbonate produced from phosphogypsum have been also analysed as shown in Table 2. The results show that Radium-226, Radium-228 and Pb-210 are the most significant radionuclide and that their concentrations have increased slightly compared to the initial values in the feed phosphogypsum although concentrations are still much less than 1Bq/g. This result is in agreement with previous reported results that most radio nuclides follow the calcium carbonate during treatment of waste gypsum [10].

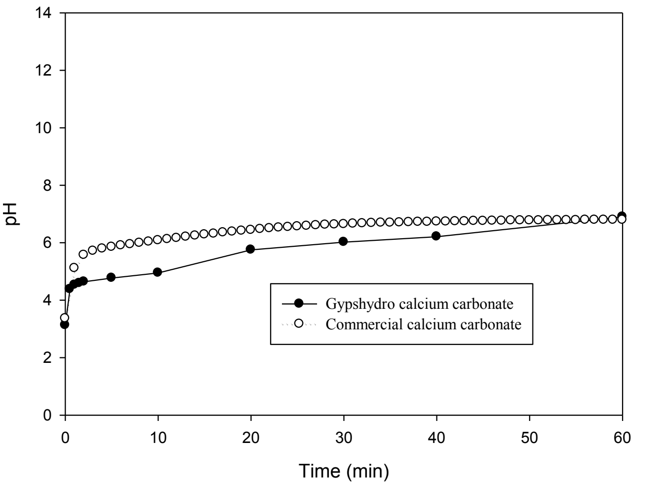

Figure 4: pH profiles during neutralization of AMD with produced calcium carbonate and commercial calcium carbonate. (Conditions: 2g calcium carbonate/1000ml AMD-315 rpm).

Conclusion

This paper constitutes the first step in an attempt to develop economical processes that could exploit and consume the phosphogypsum from the phosphate industry in South Africa for calcium carbonate production. Environmental concerns are related with the large stockpiles of phosphogypsum and their negative impact on surrounding land, water and air as most of the phosphogypsum generated each year is dumped on land or in the sea. In this study, selected parametersnamely the reaction time, the phosphogypsum slurry concentration (%), the stirring rate and the molar ratio of sodium carbonate to phosphogypsum were subjected to second order polynomial models to determine their significance on the phosphogypsum conversion to calcium carbonate using sodium carbonate. The optimum conditions for the four independent variables were derived from the experimental results and new experiments were carried out to cross-validate their liability of the optimum conditions. The conversion of Foskor phosphogypsum to calcium carbonate using sodium carbonate is estimated to be optimum if the treatment process maintains the slurry concentration at 5%, the sodium carbonate/gypsum molar ratio at 2, the stirring rate at 500 rpm and the time at 105 minutes.This study further demonstrated that the regenerated CaCO3 exhibits effective neutralisation ability during AMD pre-treatment compared to commercial laboratory grade CaCO3. The recovery of calcium carbonate from waste gypsum represents an opportunity to alleviate the high cost of the AMD treatment technologies.

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