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TECHNICAL ARTICLE

Carbothermal Reduction of Barium Sulfate-Rich Sludge from Acid Mine Drainage Treatment

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Abstract The alkali–barium–calcium (ABC) desalination process is basically an integrated lime/limestone neutralisation process combined with a sulfate removal stage using barium carbonate ($BaCO_3$), and a sludge processing stage. The $BaSO_4/CaCO_3$ sludge generated during the desalination stage is treated to recover BaS and CaO by dewatering and thermal processes, with the ultimate goal of producing sulfur and recovering $BaCO_3$. $BaCO_3$ is the main raw material used for sulfate removal and its recovery ensures that the ABC process is environmentally and financially sustainable. South Africa is also a large importer of sulfur. We evaluated the optimum conditions for the thermal treatment of $BaSO_4/CaCO_3$ sludge to recover by-products. A high temperature tube furnace was used to reduce $BaSO_4/CaCO_3$ sludge obtained from a pilot plant test conducted at a gold mine shaft. We used response surface methodology to investigate the combined effects of relevant process variables (time, temperature, and the carbon/barium sulfate ($C/BaSO_4$) molar ratio to maximize the reduction of $BaSO_4/CaCO_3$ sludge. At optimal process conditions ($T = 1{,}028$ °C; molar ratio of $C/BaSO_4 = 2.8$ mol/mol), the tube furnace yield of BaS from waste sludge was over 78.5 % after 35 min. Furthermore, the results were similar to those generated by roasting a laboratory-grade mixture of barite and calcite concentrates.

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Keywords Response surface methodology · Sludge treatment · Tube furnace

Introduction

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. The gold mining industry in South Africa (principally the Witwatersrand Goldfield) is in decline, but the post-closure discharge of acid mine drainage (AMD) represents an enormous threat. The potential volume of AMD from the Witwatersrand Goldfield alone amounts to an estimated 350 mL/day (Duane et al. 1997). A wide range of AMD treatment technologies has been developed and globally proven (Akcil and Koldas 2006), but very few remove sulfate, which is critical in arid South Africa. Moreover, in the face of global environmental challenges, AMD technologies need to integrate the treatment of the generated waste (sludge) in order to meet modern requirements of environmental protection and material utilisation efficiency. The alkali–barium–calcium (ABC) desalination process was developed in South Africa as a potential zero waste technology for AMD treatment (Akcil and Koldas 2006; Hlabela et al. 2007; Motaung et al. 2008). The ABC process was designed to neutralise AMD and remove metals and sulfate. It is basically an integrated lime/limestone process combined with sulfate removal using barium carbonate ($BaCO_3$). The major improvement in this process is that water-processing is integrated with sludge-processing to recover barium carbonate and lime, making it a low-waste technology.

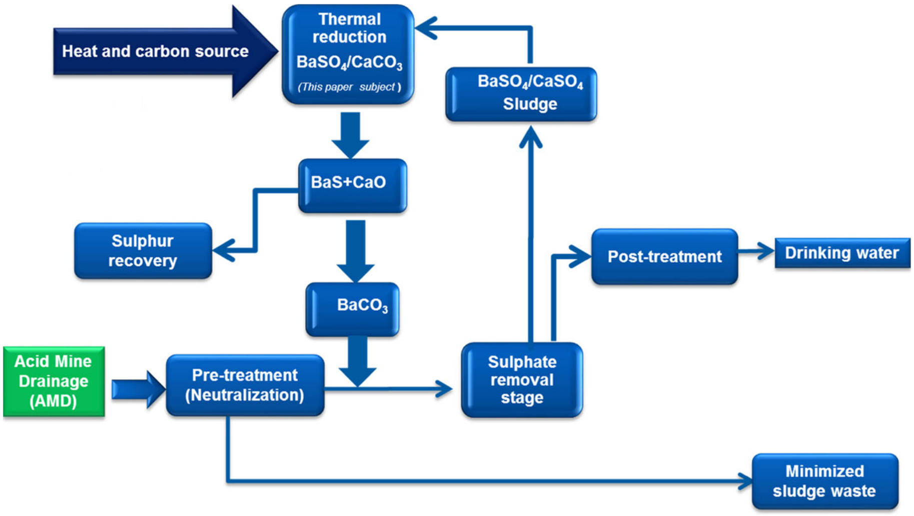

Fig. 1 Schematic diagram of the ABC chemical desalination technology

The ABC treatment process has three stages:

- Neutralisation and metal removal (Stage 1);
- Sulfate removal using $BaCO_3$ (Stage 2), and;
- Sludge processing (Stage 3).

The barium sulfate-rich sludge from Stage 2 is thermally reduced to water-soluble barium sulfide (BaS), using coal in a kiln at 1,000 °C. The BaS is hydrolysed in hot water and carbonated with CO_2 to regenerate $BaCO_3$, which is re-used. However, although the concept of the ABC process can be considered one of the most advanced for desalinating mine waters (Akcil and Koldas 2006; Hlabela et al. 2007; Motaung et al. 2008), the sludge-processing stage, which is key to its cost effectiveness and sustainability, is still not entirely resolved. For the $BaCO_3$ to be most efficient as a precipitant during the recovery cycles, it is extremely important to achieve maximum reduction of the barium sulfate to the water-soluble barium sulfide in each cycle. Thus, it is critically important within this process to establish the conditions under which the barium sulfate can be reduced most completely to BaS. To do this, we ran experiments using sludge from an ABC technology pilot plant test. The results of this study were then compared to results generated by roasting a laboratory-grade mixture of barite and calcite concentrates (Fig. 1).

Experimental Reduction of Barium Sulfate Rich-Sludge with Carbon in a Tube Furnace

Production of $BaSO_4$-Rich Sludge

The sludge used in our experiments was produced at a pilot plant that was treating 1,000 L/day of AMD containing 2,000–4,500 mg/L of sulfate that had been pumped directly from the Harmony gold mine shaft in the Western Basin, west of Johannesburg. The key step in the ABC desalination process is the sulfate removal in Stage 2, which involves the precipitation of sulfate, mainly as gypsum, to generate a $BaSO_4/CaCO_3$ sludge, according to:

Table 1 Chemical composition of the water feed and treated effluent using the ABC process on gold mine AMD in the Western Basin

Parameter	Feed (mg/L)	Treated (mg/L)
pH	3.1	7.5
Sulfate	4,510	250
Chloride	37	37
Sodium	96	95
Potassium	3	4
Magnesium	113	2
Calcium	559	30
Silica	36	6
Manganese	174	1
Iron (II)	1,100	0
Iron (III)	200	0
Aluminium	6	0
Zinc	11	0
Nickel	18	0
Cobalt	7	0

$$Ca^{2+}(aq) + SO_4^{2-}(aq) + BaCO_3(s) \rightarrow BaSO_4(s) + CaCO_3(s) \qquad (1)$$

Prior to sulfate removal, limestone and lime were added to raise the pH and remove metals, as shown in Table 1. Sludge generated in this stage, which is mainly a combination of metal hydroxides and gypsum, is collected and treated by dewatering, drying, and reduction in a different kiln. The treatment of this first sludge lies outside the scope of this paper.

Maree et al. (2004) showed that the rate of sulfate removal by gypsum crystallisation can be predicted by:

$$d[CaSO_4 \cdot 2H_2O]/dt = k[CaSO_4 \cdot 2H_2O](S)[C - C_o] \quad (2)$$

where $d[CaSO_4{\cdot}2H_2O]/dt$ represents the rate of crystallisation of gypsum, k the reaction rate constant, S the surface area of the seed crystals, C the initial concentration of calcium sulfate in solution, and C_0 the saturated concentration of calcium sulfate in solution. The higher the concentration of dissolved calcium sulfate, the higher the rate of gypsum crystallization. The low solubility of $BaCO_3$ allows a low concentration of free Ba^{2+} ions in solution and the rate of sulfate removal increases with increased $BaCO_3$ concentration (Hlabela et al. 2007). The solubility of $BaCO_3$, like $CaCO_3$, decreases with increasing pH. Therefore, it was expected that the rate of sulfate removal would be slower at higher pH, due to lower Ba^{2+} concentrations in solution.

Characterization of Feed Material

The $CaCO_3/BaSO_4$ sludge from the water stage of the CSIR ABC process pilot plant was collected. XRD analysis showed that the sample contained 57.7 % $BaSO_4$, 39.6 % $CaCO_3$ and 2.7 % $BaCO_3$ and the waste sludge was sized to less than 250 µm. Industrial coke from George (South Africa) was used with composition (%): 60.1 fixed carbon, 2.8 moisture, 10.5 ash content, 26.7 volatile matters.

Experimental Procedures

A tubular furnace made of a 750 mm long and 24 mm diameter mullite tube mounted horizontally was used for all experiments. The temperature of the furnace was controlled by using a temperature controller.

2 kg of the $CaCO_3/BaSO_4$ sludge and 98, 195 and 293 g respectively of industrial coke which was about 50 % ($C/BaSO_4 = 1$), 100 % ($C/BaSO_4 = 2$) and 150 % ($C/BaSO_4 = 3$) of the standard stoichiometric amount for the system $BaSO_4 + 2C$, were mixed thoroughly and a precisely weighed sample was placed in the tube furnace for the carbothemal reaction in the temperature range 900–1,100 °C. For the roasting of laboratory grade mixture of barite and calcite concentrates 6 g $BaSO_4$ (98 % purity), 4.3 g $CaCO_3$ (99 % purity) were mixed with industrial coke from George (South Africa) of composition shown above. Samples were weighed and placed in the tube furnace: (a) to assess the effect of temperature for molar ratio of $C/BaSO_4 = 2$ and time = 35 min and (b) to assess the effect of $C/BaSO_4$ molar ratio for temperature = 1,030 °C and time = 35 min. After the stipulated time interval the reaction was stopped by removing the sample pan from the hot zone. The cooled sample was weighed and analysed for water-soluble barium sulfide (BaS) iodometrically.

Table 2 Full factorial design and experimental results for thermal reduction of the $CaCO_3/BaSO_4$ sludge

T (A) (°C)	Time (B) (min)	$C/BaSO_4$ (mol/mol)	BaS yield (%)
900	15	1	28.64
1,000	15	1	43.16
1,100	15	1	39.42
900	30	1	30.02
1,000	30	1	43.98
1,100	30	1	40.32
900	45	1	35.28
1,000	45	1	48.06
1,100	45	1	58.66
900	15	2	43.51
1,000	15	2	70.88
1,100	15	2	68.2
900	30	2	49.85
1,000	30	2	71.35
1,100	30	2	69.01
900	45	2	53.93
1,000	45	2	66.53
1,100	45	2	64.25
900	15	3	54.64
1,000	15	3	78.28
1,100	15	3	78.38
900	30	3	66.22
1,000	30	3	70.92
1,100	30	3	67.96
900	45	3	71.48
1,000	45	3	72.1
1,100	45	3	78.66

Carbothermal Reactions of Barium Sulfate

Ravdel and Novikova (1963) have shown that the initial reduction of barite with carbon takes place according to Eq. (3) below:

$$BaSO_4 + 4C \leftrightarrow BaS + 4CO \quad (3)$$

The CO generated diffuses and reacts with barite, which is not in contact with carbon, according to (4):

$$BaSO_4 + 4CO \leftrightarrow BaS + 4CO_2 \quad (4)$$

The CO_2 produced by this later reaction diffuses back into carbon to generate more CO, according to the Boudouard reaction (5):

$$C + CO_2 \leftrightarrow 2CO \quad (5)$$

Further investigations of the kinetics of the reduction of $BaSO_4$ with coal (Lozhkin et al. 1974) have shown that the rate of reaction (5) is the limiting (controlling) step of the overall carbothermic reaction. The conversion reaction of barite to BaS is controlled by reaction kinetics, in the low temperature range (900–1,020 °C), whereas the conversion reaction can be modeled with a diffusion control model at higher temperatures (1,140–1,200 °C). Pelovski et al. (1987) studied the reduction of barium sulfate by carbon in the presence of inorganic salts such as sodium carbonate and calcium chloride and observed that these additives promote the reduction of barite. However, most of the studies mentioned above were conducted using pure grade barite concentrate.

Results and Discussions

In many industrial situations, the best combination of processing factors needs to be found. Response surface methods (RSM) can be used to help find these optimal conditions. The basic approach is to build a polynomial model of the investigated response in terms of the chosen factors. In this case, the factors of interest are the ratio of carbon to barium sulfate in the feed material, the reaction time, and the temperature. A 3-level full factorial design was used to obtain a quadratic model to estimate the process variability with BaS production yield as response. The three independent variables were each studied at three different levels, requiring a set of 27 experiments (Table 2). A multiple regression analysis of the data was then made to derive an empirical model that relates the BaS yield (%) to the independent variables.

The optimum values of the critical variables were found by analyzing surface plots. The factorial design experiments in Table 2 showed a wide variation in the BaS yield, which justified the optimization experiments. Figure 2 shows the dependency of BaS yield on the reduction time and the molar ratio of $C/BaSO_4$. The BaS yield increased with a higher $C/BaSO_4$ molar ratio to about 2.7, and thereafter decreased slightly. Figure 3 shows the dependency of BaS yield on the reduction time and the temperature. The BaS yield rose with increased temperature to about 1,025–1,030 °C and thereafter decreased. Table 3 shows that the two most important parameters affecting the yield of BaS production are the molar ratio $C/BaSO_4$ and the temperature; "Prob $> |t|$" less than 0.05 indicates model terms that are significant and values greater than 0.1 indicate model terms that are not significant. In the present work, only the linear effects of the temperature and $C/BaSO_4$ molar ratio were significant for BaS yield. The coefficient of determination (R^2) for BaS yield was calculated as 0.9344, which is very close to 1 and can explain up to 93.44 % variability of the response. The effects of the temperature and $C/BaSO_4$ molar ratio are summarized in Fig. 4, which depicts the estimated mean response as a

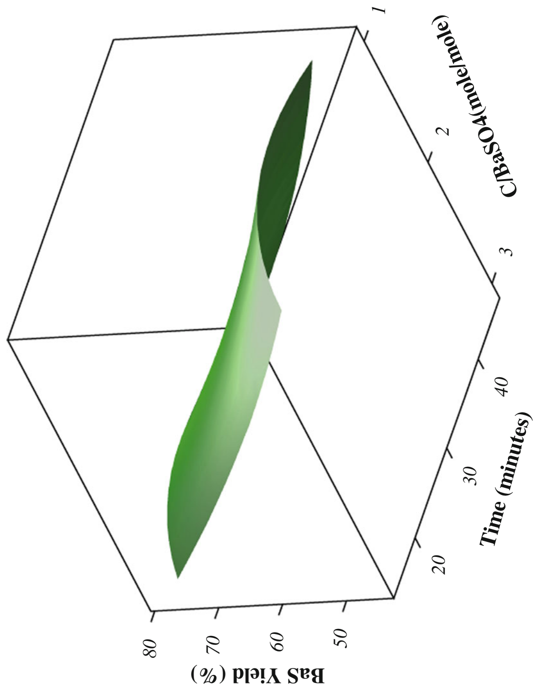

Fig. 2 Surface plot of the effect of time (min) and $C/BaSO_4$ (mole/mole) on the BaS production yield

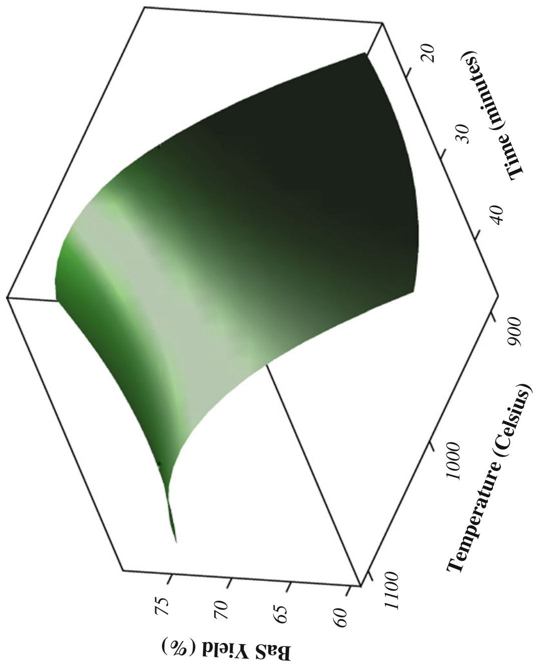

Fig. 3 Surface plot of the effect of time (min) and temperature (°C) on the BaS yield

Table 3 Analysis of variance of the response surface quadratic model obtained from experimental designs in Table 2

Term	Estimate	Std error	t ratio	Prob > |t|
Intercept	67.90	3.072	22.10	<0.0001*
Temperature (°C) (900, 1,100)	8.424	2.052	4.10	0.0063*
Time (min) (15, 45)	3.865	2.052	1.88	0.1087
$C/BaSO_4$ (mol/mol) (1, 3)	14.81	2.052	7.22	0.0004*
Temperature (°C) * Time (min)	−0.495	2.294	−0.22	0.8363
Temperature (°C) * $C/BaSO_4$ (mol/mol)	−0.405	2.294	−0.18	0.8657
Time (min) * $C/BaSO_4$ (mol/mol)	−1.095	2.294	−0.48	0.6501
Temperature (°C) * Temperature (°C)	−6.669	3.997	−1.67	0.1462
Time (min) * Time (min)	2.605	3.997	0.65	0.5386
$C/BaSO_4$ (mol/mol) * $C/BaSO_4$ (mol/mol)	−8.649	3.997	−2.16	0.0737

Asterisk means that the model term is significant

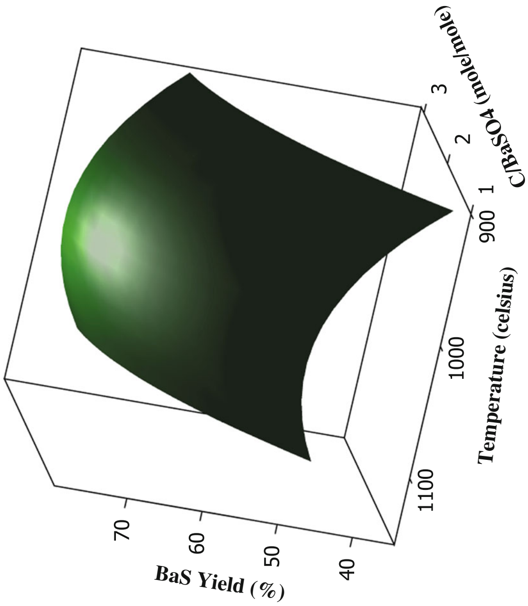

Fig. 4 Surface plot of the effect of $C/BaSO_4$ (mol/mol) and temperature (°C) on the BaS yield

surface. The high positive value of the temperature coefficient (estimate, Table 3) caused the initial upward slope, and the negative value of the coefficient for the temperature quadratic terms (estimate, Table 3) caused a slight curvilinearity, as the quadratic term of temperature in Table 3 is not significant in the model. This is evident in Fig. 3 and agrees with experimental data from an experiment conducted with a laboratory-grade mixture of barite and calcite concentrates (Fig. 5).

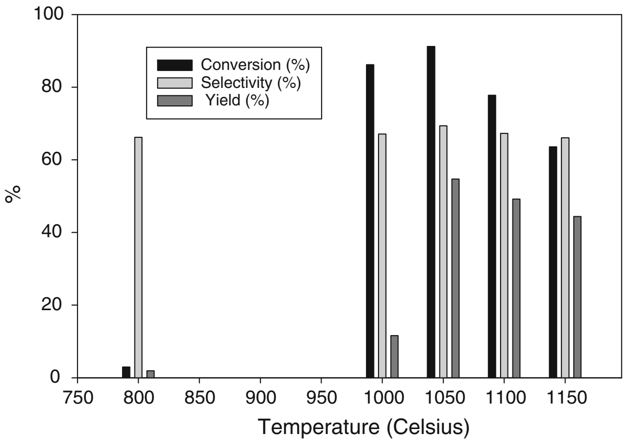

Fig. 5 Effect of temperature (°C) on $BaSO_4$ conversion, BaS selectivity from $BaSO_4$ and the tube furnace yield of BaS from $BaSO_4$. Experimental conditions: $C/BaSO_4 = 2$, Time = 35 min, 6 g $BaSO_4$ (98 % purity), 4.3 g $CaCO_3$ (99 % purity) and 1.0086 g coal (60 % purity)

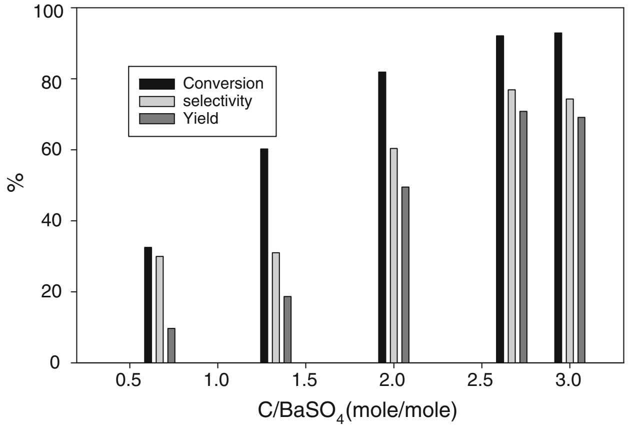

Fig. 6 Effect of $C/BaSO_4$ molar ratio on the $BaSO_4$ conversion, BaS selectivity from $BaSO_4$ and the tube furnace yield of BaS from $BaSO_4$. Experimental conditions: temperature = 1,030 °C, 6 g $BaSO_4$ (98 % purity), 4.3 g $CaCO_3$ (99 % purity), time = 35 min

The $C/BaSO_4$ molar ratio exhibited similar behavior to the temperature, with an initial upward slope due a high positive value of the $C/BaSO_4$ coefficient (Table 3), and then a very slight curvilinearity as the quadratic term of $C/BaSO_4$ in Table 3 is not significant in the model. This also agreed with the experimental results with the laboratory-grade mixture of barite and calcite concentrates (Fig. 6).

In Figs. 5 and 6, the conversion is the percentage of starting material ($BaSO_4$) converted into the desired product or by-products (ratio of barite consumed in the tube furnace/barite fed to the tube furnace), while the tube furnace yield is the percentage of $BaSO_4$ converted into BaS only (ratio of barium sulfide produced in the tube furnace/barite fed to the tube furnace). Barium sulfide selectivity from barite is the ratio of BaS produced in the tube furnace/barite consumed in the tube furnace.

Maximum yields resulted from $C/BaSO_4$ molar ratio of about 2.8 and temperature of about 1,028 °C (Figs. 5, 6); in agreement with the predicted response surface (Fig. 4).

Conclusion

We evaluated the carbothermal reduction of a sludge generated during an ABC process pilot plant demonstration. RSM was used to maximize the tube furnace yield of BaS from $BaSO_4$. The process variables included time, temperature, and the $C/BaSO_4$ molar ratio. In the optimum conditions of the process ($T = 1{,}028$ °C; molar ratio $C/BaSO_4 = 2.8$ mol/mol) the tube furnace yield of BaS from waste $BaSO_4$-rich sludge after 35 min was over 78.5 %. Comparison of the data using a laboratory-grade mixture of barite and calcite concentrates with data from the reduction of the sludge generated from the ABC pilot plant showed similar behaviors. This study provides initial optimization of the ABC thermal stage, which will ensure that the overall ABC process is a strong candidate for cost-effective treatment of mine water through valuable by-products recovery. The projected running costs of the ABC process = 4.04 R/m^3 (US\$1.00 = ZAR7.60), whereas potential income from by-products such as sulphur is projected at 3.56 R/m^3 (US\$1.00 = ZAR7.60).

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References

Akcil A, Koldas S (2006) Acid mine drainage (AMD): causes, treatment and case studies. J Clean Prod 14:1139–1145

Duane MJ, Pigozzi G, Harris C (1997) Geochemistry of some deep gold mine waters from the western portion of the Witwatersrand Basin, South Africa. J Afr Earth Sci 24:105–123

Hlabela PS, Maree JP, Bruinsma D (2007) Barium carbonate process for sulfate and metal removal from mine water. Mine Water Environ 26:14–22

Lozhkin AF, Pashcenko VN, Povar FV (1974) Kinetics of reduction of barite by roasting with carbon. J Appl Chem USSR 47:1031

Maree JP, de Beer M, Strydom WF, Christie ADM, Waanders FB (2004) Neutralizing coal mine effluent with limestone to decrease metal and sulfate concentrations. Mine Water Environ 23:81–86

Motaung S, Maree J, De Beer M, Bologo L, Theron D, Baloyi J (2008) Recovery of drinking water and by-products from gold mine effluents. Water Resour Dev 24:433–450

Pelovski Y, Ir Gruchavov, Dombalov I (1987) Barium sulfate reduction by carbon in presence of additives. J Therm Anal 32:1743

Ravdel AA, Novikova NA (1963) Reduction of barite with carbon. J Appl Chem USSR 36:1384