

Coal acid mine drainage treatment using cement kiln dust

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Abstract

Sulphurs are present in different rocks. During mining activities and the sulphur removal processes Acid Mine Drainage (AMD) may be produced, by sulphate ions (SO_4^{2-}) in solution. AMDs are the main source of pollution from mining operations and in Colombia their discharge into natural bodies of water must comply with national environmental regulations (pH between 5 and 9). Cement Kiln Dust (CKD), with calcium carbonate as its main component, from a Cementos Argos S.A. plant was used to neutralize an AMD generated through a coal bio-desulphurization process. Neutralized AMDs had pH values between 7.72 – 8.05 and the sulphates removal ranged from 67% to 70%. Precipitated sludge was dried and analyzed in order to determine its chemical and mineralogical composition. Moisture content was between 69% and 81%; this precipitated material was composed of gypsum with approximately 50% purity, as well as calcium carbonate. This composition makes it suitable for use in cement production.

Keywords: Acid Mine Drainage; Sulphate Removal; Cement Kiln Dust; Synthetic Gypsum.

Tratamiento de drenaje ácido de minería de carbón usando polvo de horno de cemento

Resumen

Los sulfuros están presentes en distintas rocas. Durante las actividades mineras y el proceso de remoción de sulfuros se pueden producir Drenajes Ácidos de Minería (DAM), con iones de sulfato (SO_4^{2-}). Los DAMs son fuente de contaminación en las actividades mineras y en Colombia su descarga en los cuerpos de agua debe cumplir las regulaciones nacionales (pH entre 5 y 9). Polvo de horno cementero (CKD), con carbonato de calcio principalmente, de una planta de Cementos Argos S.A. fue usado para neutralizar un DAM generado en la biodesulfurización de carbón. Los DAMs neutralizados tuvieron pHs entre 7,72 y 8,05 y la eliminación de sulfatos entre 67% a 70%. El precipitado se secó y analizó para determinar su composición química y mineralógica. Se encontró humedad entre 69% y 81%; yeso con un 50% de pureza aproximadamente y carbonato de calcio. Esta composición lo hace adecuado para uso en la producción de cemento.

Palabras clave: Drenaje Ácido de Minería; Remoción de Sulfatos; Polvo de Horno de Cemento; Yeso Sintético.

1. Introduction

Acid Mine Drainage (AMD) generated during coal mining operations is normally the result of the oxidation of metallic sulphur compounds, such as pyrite, which are present as impurities in coal [1]. This process may occur naturally when coal comes into contact with water and oxygen or through anthropogenic processes, i.e. desulphurization [2, 3], and can affect different parties as stated by Rahmatian [4] such as: life in water sources, the possibility of using water for human and animal consumption or irrigation, recreation, and the coal industry itself to be increased taxes to pay.

High sulphur content in coal and limestone can lead to undesirable issues in the cement production process, such as the formation of rings inside the clinker kiln [5]. Moreover after combustion it may be transformed into sulphur dioxide (SO_2), which is itself an acid rain precursor gas [6].

In a research project conducted by Cementos Argos S.A. (in cooperation with Universidad Nacional de Colombia – Sede Medellín and Servicio Nacional de Aprendizaje, SENA) which aimed to bio-desulphurize coal with high sulphur content, it was discovered that the leachates that were generated had high sulphate content and low pH values, and will require treatment before being discharged into any body of water.

The search for adequate AMD treatment methods has been the subject of various research initiatives. The results of this research demonstrated that limestone and/or quicklime can be used to neutralize the AMD, while removing sulphates and precipitating synthetic gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) [7-9] at a low cost. Most recently, some researchers have started using microorganisms to treat AMD, alkaline by-products from coal combustion [10-11] and natural zeolites [12]. Yet quicklime still remains as the most popular neutralizer, however its use comes at a high environmental cost as CO_2 is released during the production process.

Cement kiln dust (CKD) is a powder collected in electrostatic precipitators after the clinkerization process. In many cement plants it is considered to be a waste material, as its reintroduction to the kiln can increase the alkali content of cement. Furthermore such re-introduction can lead to rheological changes inside the kiln, which can have an adverse effect on the clinker burning process [5]. Due to these limitations the CKD is often disposed of in abandoned mines, open pits or landfills. The large volumes produced, as well as its fine particle size, make it difficult to handle. Over the years different methods have been proposed for the use of CKD, the most common of which include soil stabilization, its use as an additive for blended cement and as fertilizer, the solidification/stabilization of hazardous wastes and municipal bio-solids and, as a raw material used in the production of calcium hydroxide ($\text{Ca}(\text{OH})_2$) slurries to be used as neutralizer in the treatment of acidic wastewater [13]. In many of these applications, it has been found that sulphate ions contained in the CKD have the potential to negatively affect its performance by reacting with the calcium contained within it [14].

The current research focuses primarily on solving two environmental problems: neutralizing AMDs and reusing CKDs. In addition, potential ways of utilizing gypsum precipitated during the neutralization process were also explored.

2. Materials and methods

2.1. Materials used

Several samples of a clear, unfiltered AMD were obtained from the coal bio-desulphurization process. A CKD sample from an Argos Cement plant located in the north of the Colombia was also obtained. A clinker sample from the same cement plant, gypsum mined in the Dominican Republic (YD), water and normalized Ottawa sand were also used.

2.2. Analytical methods

A pH meter was employed to determine the pH of the AMD and the neutralized samples (Schott Handylab pH 11). Neutralization tests were conducted using a magnetic stirrer with heating elements and thermocouple temperature control (Corning PC-420D). A spectrophotometer (Thermo Genesis 10 UV) was used to measure the sulphates' concentration in AMD before and after the treatment. An analytical balance (Lexus Mix-H) was used to measure the weight of the samples. Different techniques were used to determine the chemical and mineralogical composition of the precipitated

material and the CKD, such as X-Ray Diffraction (XRD), which was carried out using a PANalytical X'Pert PRO equipment, in a 2θ interval between 4° and 70° with a step of 0.02° and an accumulation time of 30 s to room temperature, with copper lamp. Fourier Transform Infra-Red Spectroscopy was carried out using a Shimadzu 8400S. X-Ray Fluorescence was carried out using a Philips XCEM 1660. Scanning Electronic Microscopy with Energy Dispersive X-Ray Spectroscopy was carried out using a JEOL JSM 5910LV to 15kV, and Thermo Gravimetric Analysis (TGA) that was carried out using a Hi-Res TGA 2950 Netchz equipment, using an alumina crucible, N_2 atmosphere and a heating rate of $20^\circ\text{C}/\text{min}$ up to 950°C .

The ASTM standard ASTM C 150 / C150M – 12 [15] was followed in order to compare cement samples that had been prepared at the laboratory level, using the precipitated material to assess the behavior of the cement.

2.3. Bench-scale experiments

Tests to neutralize the AMD with CKD were conducted based on an experimental design (two level fractional factorial design 2^{4-1} with a central point) [16] that included four factors in two levels each: rapid mix (800-1000 rpm), slow mix at 40 rpm (10-20 min), temperature (25 - 35°C), and amount of CKD (20-55 g). The experimental plan was composed of nine tests to assess the sulphates' concentration in the AMD, which had been treated with CKD (Table 1).

Initially AMD samples were homogenized in the magnetic stirrer, followed by measurements of pH values and sulphate content to establish the baseline parameters. Subsequently, 500 mL of the sample were placed in each of nine beakers before neutralization. Every beaker was then placed on the magnetic stirrer for one minute on rapid mix cycle (800-1000 rpm) to mix the CKD according to the experimental design. A slow mix at 40 rpm was then held for 10 or 20 minutes, depending on each test, in order to allow the material resulting from the neutralization process to precipitate. The beakers were covered with a plastic film to prevent dust from entering and pH was measured twice during the test: once at the end of the slow mixing cycle and once again after 192 hours.

At this point two phases were clearly identifiable in each beaker: precipitated and clarified. Sulphates and pH were measured in the clarified water after being drained from each beaker, and the excess water from the precipitated

Table 1.
Experimental design

Test	Rapid mix (rpm)	Slow mix 40 rpm (min)	Temperature ($^\circ\text{C}$)	CKD (g)
1	1000	10	35	20
2	800	20	25	55
3	800	10	35	55
4	1000	10	25	55
5	1000	20	25	20
6	900	15	30	37.5
7	1000	20	35	55
8	800	20	35	20
9	800	10	25	20

Source: The authors

sludge was evaporated at a temperature of 45 °C, so as to avoid mineralogical changes in the precipitated material [17-18], until its weight remained constant (less than 0.1% weight variation), in order to determine the moisture of the precipitated material. This material was then characterized following the methods mentioned in section 2.2. Finally, two types of cement were prepared in the laboratory (one with the precipitate and the other using Dominican gypsum) in order to compare them and to preliminarily assess their performance based on the ASTM standards mentioned before.

3. Results and discussion

3.1. CKD composition

The chemical characterization of CKD by XRF showed that the highest weight percentage in the sample was found in calcium oxide (CaO), which falls within the range reported by Mackie *et al.* [14]. Loss on ignition (LOI) is related to the CO₂ that is released and, taking into account that CKD was dry, it may be deduced that this material still contains unreacted limestone (CaCO₃) after leaving the clinker kiln, which in turn indicates that this material has neutralizing potential (Table 2).

The FTIR analysis of the CKD is shown in Fig.1. The most representative bands correspond to carbonate vibrations (labeled as CO₃). The strongest of these bands is over 1400 cm⁻¹, and there is also a narrow band around of 873 cm⁻¹, as well as a weak band with two peaks between 2875 cm⁻¹ and 2990 cm⁻¹. These values are similar to those reported by different authors [19-21]. A small amount of sulphur, represented by sulphate bands (labeled as SO₄) and a minor quantity of quartz (labeled as Qz) were also found.

The semi-qualitative XRD result, based on a comparative analysis with X'Pert HighScore® database (Fig. 2), confirmed that calcium carbonate was the main component of the CKD (shown as calcite). Two small quartz peaks are also visible in the XRD pattern, however, there were no peaks detected for minerals containing sulphates, which may have been masked by the major peaks, especially, if they are at low percentages (1 to 3%).

The TG-DTG curves are shown in Fig. 3. In the TG curve a mass loss between 600 °C and 800 °C can be observed, whereas in the DTG curve a peak representing a maximum of 771.86 °C can be seen. It is approximately at this temperature that carbon dioxide is volatilized from the calcium carbonate sample [18]. Therefore, using loss percentages, calcium carbonate content was calculated, confirming that it is a main component of the CKD.

Table 2. Chemical characterization of CKD by XRF.

Oxide	Content (%)
SiO ₂	7.8
Al ₂ O ₃	3.2
Fe ₂ O ₃	2.8
CaO	48.2
MgO	0.4
SO ₃	0.4
K ₂ O	0.2
Na ₂ O	0.0
LOI	36.5

Source: The authors

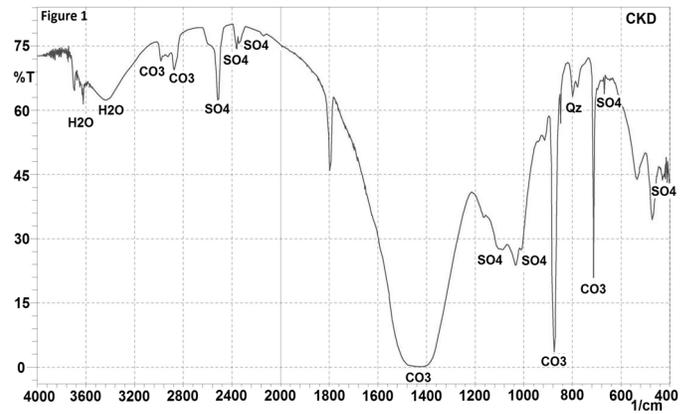


Figure 1. Infrared spectrum of the CKD (Transmittance)
Source: The authors

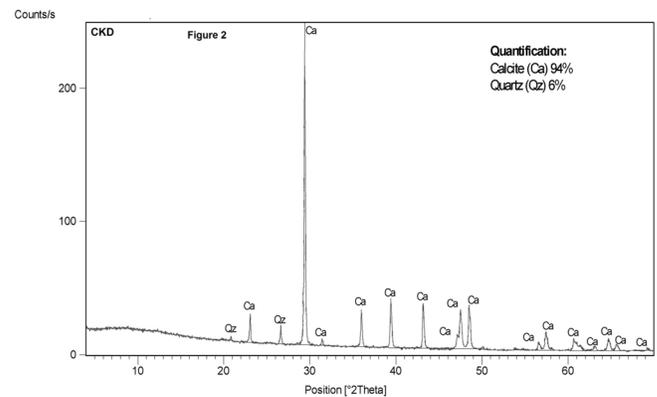


Figure 2. XRD pattern of the CKD.
Source: The authors

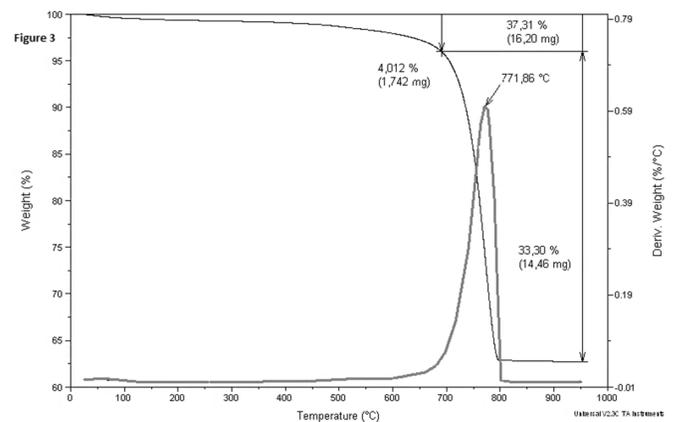


Figure 3. TG-DTG Curves of the CKD.
Source: The authors

3.2. AMD neutralization

After the mixing stage, and before the addition of CKD, sulphate concentrations were measured in the initial AMD samples. The concentration obtained in each beaker was used to calculate the removal of sulphates (Table 3), along with the corresponding pH values, which were measured

before and after neutralization.

After 192 hours the pH remained within the permissible range (5 - 9 units), as dictated by Colombian environmental regulations. There was sulphate removal of over 67% in all samples. Samples 3 and 5 had higher removal (72%) and sample 5 was closer than sample 3 to the neutral pH values. Sample 5 was chosen to be characterized along with the original AMD in an external laboratory in order to determine additional environmental parameters, such as conductivity, acidity, solid content and the presence of iron, manganese and zinc (Table 4).

Conductivity decreased after neutralization, which could be related to the removal of solids and metals from the AMD. As can be seen in Table 3, the biggest fraction of the Total Solids corresponded to Dissolved Solids, before and after neutralization. There was more than 93% precipitation in manganese, zinc and iron, which is similar to the findings of Mackie and Walsh [22].

3.3. Precipitate composition

The hypothesis of this research aimed to demonstrate that precipitated material could be considered synthetic gypsum, since the reaction occurred in an aqueous solution. Thus the analyses of properties such as Moisture content, XRD, TG, FTIR, XRF and SEM were conducted to verify this claim.

Table 3. Removal of sulphates and change in pH after neutralization of AMD with CKD.

Test	AMD Sulphates Concentration (mg/L)	Clarified Water Sulphates Concentration (mg/L)	Sulphate Removal (%)	AMD pH	Clarified Water pH (after 192 hours)
1	30204.62	10092.41	67	1.75	8.03
2	30204.62	9075.91	70	1.75	7.93
3	30204.62	8495.05	72	1.75	8.05
4	30204.62	8930.69	70	1.75	7.86
5	30204.62	8495.05	72	1.75	7.77
6	30204.62	8858.09	71	1.75	7.84
7	30204.62	8930.69	70	1.75	8.00
8	30204.62	9366.34	69	1.75	7.89
9	30204.62	8640.26	71	1.75	7.72

Source: The authors

Table 4. Characterization of sample 5 before and after neutralization.

Parameter (units)	AMD	Neutralized AMD	Removal (%)
Conductivity ($\mu\text{S}/\text{cm}$)	25250	10230	59.49
Total Acidity (mg CaCO_3/L)	11850	34	99.71
Total Iron (mg Fe/L)	2530	<0.050	100.00
Total Manganese (mg Mn/L)	14.30	0.868	93.93
Total Zinc (mg Zn/L)	3.93	0.015	99.62
Total Dissolved Solids (mg/L)	27422	12548	54.24
Total Solids (mg/L)	27510	12602	54.19

Source: The authors

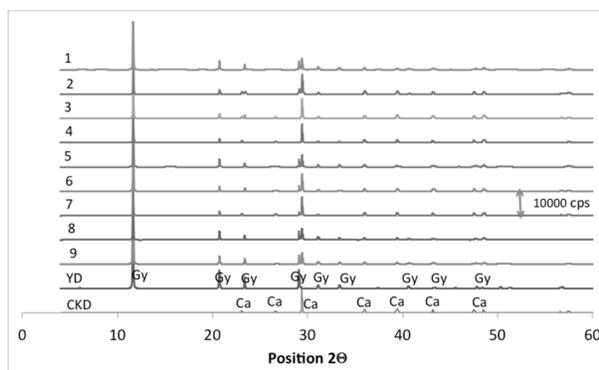


Figure 4. XRD patterns for precipitated sludge, CKD and YD. (Y axis scale is variable. Gy: di-hydrated gypsum tag, Ca: calcium carbonate tag). Source: The authors

3.3.1. Moisture content

After dehydration at 45°C the moisture content of precipitated sludge ranged between 69% and 81%. According to Aubé's findings [7] these percentages may vary between approximately 70% and 99%, which is consistent with the findings of this research.

3.3.2. X Ray Diffraction (XRD)

Fig. 4 shows diffraction patterns (XRD) for the nine samples, previously sieved between -200 and +325 meshes. CKD and Dominican gypsum (YD) patterns were also included in order to compare the representative peaks of the gypsum and calcium with the peaks of the precipitate.

Dominican gypsum (YD) showed four main peaks on the 2θ axis. The position of these peaks was similar to those reported in the X'Pert HighScore® software database for di-hydrated gypsum. Diffraction patterns for the nine samples matched the positions of the di-hydrated gypsum, and calcium carbonate peaks were also found to match the positions reported in the literature [23]. The precipitated samples showed two double peaks at the gypsum and calcium carbonate positions, one smaller between 23° and 24° 2θ positions and the more representative pair between 29° and 30° 2θ positions. This demonstrates that gypsum was produced but there is still some unreacted calcium carbonate. From Fig. 4 it can be deduced that the highest peaks of gypsum are related to the lowest peaks of calcite in the precipitated material (samples 1, 5, 8 and 9). After comparing each sample against the X'Pert HighScore® database, it was discovered that samples 5 and 9 had the highest percentage of gypsum, however the difference between them was the absence of quartz in sample 5.

3.3.3. X Ray Fluorescence (XRF)

Results obtained by XRF showed that samples 1, 5, 8 and 9 had the higher sulphur percentages, shown in Table 5 as SO_3 , which confirms the information obtained through XRD analysis. Compared to CKD the precipitated samples showed an increase in SO_3 percentage and a decrease in

CaO, which could indicate that sulphur reacted with calcium and in turn precipitated as gypsum. There was an increase in iron and magnesium oxide content in the precipitated material after the neutralization process, affirming that the metals were removed with the addition of CKD.

3.3.4 Thermo Gravimetric Analysis (TG)

This method was used to determine the percentage of gypsum in the precipitated material. Previous studies have demonstrated that when gypsum is dehydrated to hemihydrate

there is an initial mass loss of 15% close to 150° C. There is then a mass loss of 5% in the dehydration of the hemihydrate at around 200° C [24]. Dominican gypsum showed a mass loss of 15.68% around 150° C and precipitated samples 1, 5, 8 and 9 presented close to a 10% mass loss at that temperature. The other samples exhibited a loss in mass of less than 6%. At around 750° C there was further loss of mass when carbon dioxide is released through volatilization, thus confirming the presence of Calcium Carbonate after neutralization in the precipitated material (Table 6).

Table 5. XRF analysis of samples.

Sample	Oxide Content (%)								
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	LOI
YD	4.29	0.96	0.68	29.81	2.06	41.41	0.14	0.04	20.61
CKD	7.88	3.21	2.80	48.23	0.49	0.44	0.20	0.00	36.53
Sample 1	5.57	3.25	6.56	32.22	1.36	24.05	0.24	0.12	26.63
Sample 2	7.05	3.17	4.05	40.09	1.16	12.99	0.25	0.10	31.15
Sample 3	6.95	3.15	3.82	39.83	1.54	13.63	0.27	0.16	30.65
Sample 4	7.20	3.23	3.91	40.78	1.27	12.25	0.25	0.10	31.01
Sample 5	5.98	3.39	6.36	33.55	1.28	22.49	0.24	0.13	26.59
Sample 6	6.62	3.24	4.80	38.02	1.28	16.42	0.25	0.12	29.25
Sample 7	7.13	3.15	3.90	40.58	1.35	12.35	0.26	0.11	31.18
Sample 8	5.58	3.22	6.50	32.71	1.27	23.88	0.24	0.13	26.48
Sample 9	5.59	3.28	6.49	32.84	1.27	23.59	0.24	0.11	26.59

Source: Source: The authors

Table 6. Gypsum and calcium carbonate content in the samples.

Sample	Gypsum content (%)	Calcium carbonate content (%)
YD	75	13
CKD	0	76
1	50	28
2	30	68
3	25	56
4	25	56
5	48	32
6	32	48
7	25	56
8	50	29
9	51	29

Source: The authors

3.3.5. Fourier Transform Infrared Spectrometry (FTIR)

This technique was used to qualitatively complement the XRD, XRF and TG analyses. Precipitated samples 1, 5, 8 and 9 showed representative bands in the vibration spectrum in the normal positions for carbonates, sulphates and quartz. These bands were labeled as follows: calcium carbonate vibrations as CO₃, di-hydrated gypsum vibrations as SO₄, di-hydrated gypsum water molecule vibrations as H₂O and quartz vibrations as Qz. Fig. 5 shows the spectrum obtained for precipitated sample 5.

3.3.6. Scanning Electron Microscopy (SEM)

As can be seen in Fig. 6, precipitated samples showed mainly crystals with a tabular habit, and there is also a crystal

that could match the description of crystal twinning (simple

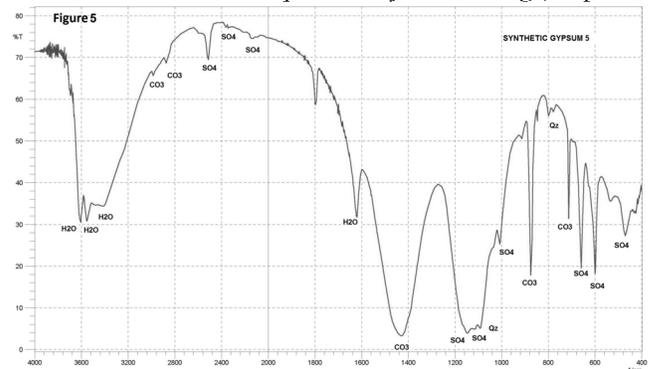


Figure 5. FTIR spectrum precipitated sample 5.

Source: The authors

twin), as described by Nesse [17]. One can observe in the enlarged image how gypsum accumulates on the same crystal to increase its size. With regards to size, synthetic gypsum crystals were smaller than those in mined gypsum, which may be related to their origin.

3.3.7. Clinker blended with synthetic gypsum

Table 7 shows the time of setting for the two cement types prepared in the laboratory, the first using clinker and Dominican gypsum (control cement) and the second using clinker and synthetic gypsum. These results complied with ASTM C 150/C 150M-12 minimum and maximum time of setting standards for Type I cement.

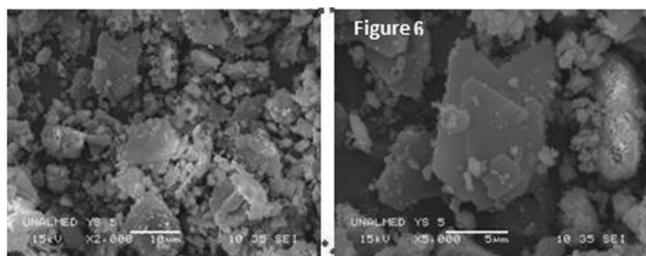


Figure 6. Sample 5 SEM Image.

Source: The authors

Table 7.

Time of setting.

Cement type	Initial time of setting (min)	Final time of setting (min)
Control cement	128	170
Synthetic gypsum cement	139	200
ASTM C-150/C 150M-12 (type I cement)	45	375

Source: The authors

Table 8.

Compressive strength.

Curing time (days)	Control cement (MPa)	Synthetic gypsum cement (MPa)	ASTM C-150/C 150M-11 (type I cement)
3	15.9	14.5	12
7	22.7	22.3	19
28	35.0	28.7	---

Source: The authors

Table 8 shows the compressive strength found in mortars that were prepared with the two cements. The standards are the minimum permitted values.

Synthetic gypsum caused a slight delay in both times of setting and developed very similar values for compressive strength. This could be related to its reactivity and also to the effect of contaminants that precipitated with it. The delay could also allow a time increase for workability. We can therefore say that the synthetic gypsum obtained in this process can be used in the manufacture of Portland cement, replacing gypsum obtained through mining activities.

4. Conclusions

Characterization by XRF, FTIR, XRD, and TG-DTG showed that CaO and CaCO₃ were the main components in CKD, which indicates that this material has neutralizing potential and can be used to treat AMD. This confirms earlier studies in which this material is proposed for the treatment of acidic waste water, including metals such as Iron and Zinc.

It was confirmed that higher turbulence improves the neutralization reaction between AMD and CKD and, consequently, the precipitation of synthetic gypsum can occur.

Under the conditions of this project, approximately 1.5 g of CKD were required to react with 1.0 g of sulphates in an AMD sample, producing synthetic gypsum that can be exploited industrially. It is important to highlight that these

quantities are not a definitive recipe, as they correspond to the specific conditions of this research. It is possible that CKD can also be used to treat acid effluents from other industrial processes in an economically efficient way.

Although acidity removal and pH increase to neutral values proved to be effective, it is recommended that a combination of CKD and lime could be tested in future researches, and which could potentially improve AMD neutralization.

Results showed that synthetic gypsum obtained under these research conditions can be used to produce cement, and the values found for time of setting and compressive strength complied with ASTM standard specifications.

As a general conclusion to this research, it can be stated that there are many possibilities to prevent environmental pollution through the manipulation and optimization of industrial processes, in order to find new uses for the by-products and residues from the intermediate and end stages.

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References

- Marcello, R.R., Galato, S., Peterson, M., Riella, H.G. and Bernardin, A.M., Inorganic pigments made from the recycling of coal mine drainage treatment sludge. *Journal of environmental management*, 88, pp. 1280–1284, 2008.
- Cara, J., The biodesulphurization of a semianthracite coal in a packed-bed system. *Fuel*, 82, pp. 2065–2068, 2003.
- Evangelou, V., Pyrite microencapsulation technologies: Principles and potential field application. *Ecological Engineering*, 17, pp. 165–178, 2001.
- Rahmatian, M., The incidence of environmental degradation: A case study of acid mine drainage. *Journal of environmental management*, 30, pp. 145–155, 1990.
- Peray, K.E., *The Rotary Cement Kiln*, Second. Ed. Chemical Publishing Co., Inc., New York, USA, 1986.
- Doménech, X., *Química atmosférica, origen y efectos de la contaminación*. Miraguano ediciones, Madrid, España, 1991.
- Aubé, B. and Zinck, J., Lime Treatment of Acid Mine Drainage in Canadá, in: *Brazil-Canada Seminar on Mine Rehabilitation*. Brazil-Canada Seminar on Mine Rehabilitation, Florianópolis, 2003, pp. 1–12.
- Cravotta III, C., Limestone drains to increase pH and remove dissolved metals from acidic mine drainage. *Applied Geochemistry*, 14, pp. 581–606, 1999.
- Kalin, M. and Harris, B., Chemical precipitation within pyritic waste rock. *Hydrometallurgy* 78, 209–225, 2005.
- Bulusu, S., Aydilek, A.H. and Rustagi, N., CCB-based encapsulation of pyrite for remediation of acid mine drainage. *Journal of hazardous materials*, 143, pp. 609–619, 2007.
- Sheoran, A.S. and Sheoran, V., C.R.P. Bioremediation of acid-rock drainage by sulphate-reducing prokaryotes: A review. *Minerals Engineering*, 23, pp. 1073–1100, 2010.
- Calvo, B., Canoira, L., Morante, F., Martínez-Bedia, J.M., Vinagre, C., García-González, J.E., Elsen, J. and Alcantara, R., Continuous

- elimination of Pb²⁺, Cu²⁺, Zn²⁺, H⁺ and NH₄⁺ from acidic waters by ionic exchange on natural zeolites. *Journal of hazardous materials*, 166, pp. 619–627, 2009.
- [13] Bhatti, J.I., *Alternative Uses of Cement Kiln Dust*. 1995.
- [14] Mackie, A., Boilard, S., Walsh, M.E. and Lake, C.B., Physicochemical characterization of cement kiln dust for potential reuse in acidic wastewater treatment. *Journal of hazardous materials*, 173, pp. 283–291, 2010.
- [15] ASTM International. *ASTM C 150 / C150M - 12 Standard Specification for Portland Cement*. USA, 2012.
- [16] Gutiérrez, H. y De La Vara, R., *Análisis y diseño de experimentos*, Segunda ed. McGraw-Hill/Interamericana Editores S.A. de C.V., México D.F., 2008.
- [17] Nesse, W.D., *Introduction to mineralogy*. Oxford University Press, New York, USA, 2000.
- [18] Ramachandran, V.S., Paroli, R.M., Beaudoin, J.J. and Delgado, A.H., *Handbook of Thermal Analysis of Construction Materials*. Noyes Publications/William Andrew Publishing, New York, USA, 2002.
- [19] Anbalagan, G., Mukundakumari, S., Murugesan, K.S. and Gunasekaran, S., Infrared, optical absorption, and EPR spectroscopic studies on natural gypsum. *Vibrational Spectroscopy*, 50, pp. 226–230, 2009.
- [20] Böke, H., Quantification of CaCO₃-CaSO₃·0.5H₂O-CaSO₄·2H₂O mixtures by FTIR analysis and its ANN model. *Materials Letters*, 58, pp. 723–726, 2004.
- [21] Jun Chu, K., Seun Yoo, K. and Tae Kim, K., Characteristics of gypsum crystal growth over calcium-based slurry in desulfurization reactions. *Materials Research Bulletin*, 32, pp. 197–204, 1997.
- [22] Mackie, A.L. and Walsh, M.E., Bench-scale study of active mine water treatment using cement kiln dust (CKD) as a neutralization agent. *Water research*, 46, pp. 327–334, 2012.
- [23] Santagata, M., Sreekrishnavilasam, A. and King, S., Characterization of fresh and landfilled cement kiln dust for reuse in construction applications. *Engineering Geology*, 85, pp. 165–173, 2006.
- [24] Payá, J., Borrachero, M. V., Bonilla, M. and Monzó, J., The use of thermogravimetric analysis technique for the characterization of construction materials, the gypsum case. *Journal of Thermal Analysis and Calorimetry*, 91, pp. 503–509, 2008.
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