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Evaluation of the use of TiO_2 industry red gypsum waste in cement production

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ABSTRACT

This work analyzes and evaluates the main mechanical, elastic and thermodynamic properties of cements manufactured with different proportions of red gypsum (RG), a waste generated by the titanium dioxide industry. The results show that red gypsum can be used as a safe substitute for natural gypsum in the manufacturing of commercial cements with no reduction in quality. In addition, the mobility of the original pollutants in red gypsum is negligible in the cements made from this waste, with the quantities of leached pollutants similar to those measured in standard reference cements formed with natural gypsum.

1. Introduction

Industrial wastes are being used within the cement industry [1–5], either as an ingredient for clinker production or as an addition to clinker for cement production.

The production of titanium dioxide pigments by the "sulphate method" uses ilmenite (rich in titanium and iron) as raw material which, after grinding, is exposed to sulphuric acid at 98% for its dissolution. From the resulting acid solution, the titanium is precipitated as titanium dioxide (the basis of the final pigments), and the process generates a weak acid effluent in the final pigment washing stages. This effluent is processed via a neutralization plant. In this stage lime, or limestone, is added to the weak acid stream, generating the red gypsum (RG) waste, which is then separated by filtration.

This process gives RG with a high concentration of SO_3 and CaO, being $CaSO_4{\cdot}2H_2O$ the main crystalline phase [6,7]. Neither is it surprising, taking into account the origin of this weak acid, to find a high TiO_2 content in this waste (around 5%), the recovery of which could lead to a substantial improvement in the industrial process. RG also has high concentrations of iron hydroxides (~8%), as detailed in previous investigations [6], which explain its characteristic reddish colour.

As far as we know, the red gypsum generated in the TiO_2 pigment factories around the world is not treated as dangerous waste, and is neither utilized nor commercialized in any way. This is the case of the RG produced at a TiO_2 factory in the city of Huelva (southwestern Spain) where around 70,000 tons of this waste are produced annually, and which is disposed of in a controlled industrial waste repository about 70 km from the factory.

The RG management policy generates costs that affect the competitiveness of the Huelva factory, so the company decided to assess the valorization options of this waste; the development of this paper was an important part of that evaluation.

In the cement industry, large quantities of natural gypsum (NG) are used in cement production as a set retardant, by adding it to the clinker in a proportion that ranges from 3% to 5% [8]. There are several industrial by-products classified also as retardants (e.g. Phospho-, Boro-, citro- and desulpho-gypsum) [8–11]. With this in mind, and knowing that calcium sulphate is the main component in RG, we have analyzed the possibility of using RG as a substitute for natural gypsum in the production of cement.

Obviously, cement production based on waste from other industrial activities must be undertaken with caution. In this sense, the physical and chemical properties of the new cement generated should be comparable to those of normal cement. One goal should be a reduction in the environmental impact of the cement production and use [12].

The main objective of this work is to analyze the viability of using RG in cement production and to examine whether the use of this waste in various proportions modifies the properties of the cement generated. The cements produced with this waste material are checked for compliance with quality standards and regulations

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regarding the fresh and hardened properties of formed cement pastes, including measurements of calorimetry and substance leaching potential. Comparisons are made to cement pastes formed from Ordinary Portland Cement (OPC).

2. Materials and methods

2.1. Materials

The sample of red gypsum used in this study was collected from a titanium dioxide production plant 12 km from the city of Huelva, in south-western Spain. After collection, the red gypsum sample was dried at 45 °C to avoid structural water loss.

As the objective of our work was to ascertain whether RG could substitute natural gypsum as a set retarder in the manufacture of cement (avoiding the flash set effects), mixtures of varying percentages of RG were added to conventional clinker. The mixtures studied were: YA (97.5% Clinker-2.5% red gypsum), YB (95% Clinker-5% red gypsum) and YC (90% Clinker-10% red gypsum). The properties of these mixtures (physical behaviour of the matrix formed, calorimetric analysis, mechanical resistances, leaching and volumetric tests) were compared with the properties of commercial cement (CEM). This reference cement (CEM) is characterized by a compressive strength category of 52.5 N/mm^2, and is composed of a mixture of clinker (97%) and natural gypsum (3%). The clinker used for the three mixtures with RG is a standard Portland clinker [8].

2.2. Methods to evaluate the RG cements generated

2.2.1. Calorimetry

During cement paste hydration, transitions occur from high to low energy states, the excess energy being liberated in the form of heat. The sudden build-up of heat in the system can lead to a rapid evaporation of water which could lead to cracks in the mortar.

An isothermal conduction calorimeter (model THERMOMETRIC 3116/3239 TAM) was used in the calorimetric analyses. All the analyses were performed at a temperature of 25.0 ± 0.5 °C, taking distilled water as a reference system, with five grams of the sample for analysis added to the calorimeter. Calorimetric analyses of the three RG cements were carried out to determine the total heat liberated in their hydration processes, as well as the velocity of heat liberation.

2.2.2. Measurement of setting times and water/cement (W/C) ratio

The water/cement ratio (W/C) is probably the most important parameter in the technology of cement materials such as concrete and mortar. In studies of concrete, the compressive strength is known to vary inversely to the W/C ratio [13].

To calculate the W/C ratios, a normalized Vicat apparatus with a rod 50 mm in length and 10 mm in diameter was used, and various moulds of the three RG mixtures were made with different W/C proportions. The moulds were 40 mm in height, and shaped as a truncated cone with lower and upper diameters of 70 and 80 mm, respectively. For each mixture, the "optimum" W/C ratio corresponded to the penetration of the rod in the mould to a depth of 34 mm.

Another important property of commercial cement is its setting time. Natural gypsum is added during the grinding of the Portland clinker to delay the quick setting of the cement [14]. This means that concrete or mortar made with a binder should have a setting time long enough for concrete or mortar transport time.

The setting times of the three cements formed by using different proportions of red gypsum as an additive were also obtained with a Vicat apparatus equipped with a normalized noodle with a 1.13 mm diameter. All the cements were analyzed as pastes formed with the previously established optimum W/C ratios. The protocol used to measure the setting times is based on the study of the depth of penetration of the noodle in the mould at different positions (UNE-EN 196-3). At time zero, the noodle penetrates to the base of the mould. When the noodle has penetrated to a depth of 4 mm above the base, the hardening of the cement is considered to have started (initial setting time). When the noodle has penetrated only 0.5 mm into the mould, the cement hardening is deemed to have finished (final setting time).

2.2.3. Granulometry

The granulometric analyses have been performed by using a Sympatec diffractometer that operates in a range between 0.90 and 175 μm. This technique is based on the incidence of a monochromatic laser beam through a non-reactive liquid carrying the sample to be analyzed. To provoke the total dispersion of the samples in the non-reactive liquid, isopropylic alcohol was used to remove the electronic and Van der Waals forces between the particles.

2.2.4. Volumetric stability tests

The Le Chatelier test was performed in accordance in order to analyze the possible risks of short-time expansion (regulation UNE-EN 196-3), since hydration of calcium or magnesium oxide free could affect the red gypsum cements formed. This test is based on the use of a small cylindrical mould opened at the generatrix and closed with two noodles at a fixed distance from each. The mould is filled with a paste from the cement to be analyzed (the paste was formed at the optimum W/C ratio established previously), stored in a humidity chamber for 24 h. Finally, one half of the mould was submerged in boiling water for 3 h, and the other half in water at room temperature for 7 days. The increase in the distance between the ends of the two noodles gives a value that can be used as a reference for the expansion of the cement.

2.2.5. Mechanical resistant tests

Mortars (sand and cement mixed in a 3:1 proportion) were used to conduct tests to evaluate the compressive and flexural strength of the cements fabricated with RG. These mortars were made from sand with a SiO_2 content of about 99% mass.

Once the different mortars were made, their binding and compressive resistances were measured in prismatic test samples ($40 \times 40 \times 160$ mm) 2 and 28 days after their formation, in line with regulation UNE-EN 196-1. Flexural resistance was calculated by applying the centered and concentrated loads method to the prismatic samples, while compression was measured with the broken prismatic samples from the flexural tests on surfaces of 40×40 mm.

2.2.6. Retraction tests

Mortar samples (under the same conditions and sand/cement proportions as for the mechanical tests) were made to fix the linear retraction in the RG cements that occurs due to their progressive dryness. The mortars were tested in accordance with regulation ASTM C 596-89. Special moulds were filled with the mortar samples for this purpose, as described in this protocol.

2.2.7. Mobility leaching test

To evaluate the mobility of the pollutants in the manufactured cement after adding RG, the US EPA standard leachability test [15], or TCLP (Toxicity Characteristic Leaching Procedure), was performed. A suitable TCLP test extraction fluid was selected based on the pH sample, which was evaluated as prescribed in the standard procedure. A 50 mL aliquot of the leachate was treated using a concentrated nitric acid solution (3 mL) to keep the pH sample low (<pH 2) and then analyzed for metals by the ICP-MS technique.

The ICP-MS technique was also used to determine the trace elements in the RG sample. In this case, the results were achieved following the total dissolution of the samples by microwave acid digestion (hydrochloric, hydrofluoric, nitric and percloric acids), and their subsequent dilution for placement in the ICP-MS system as 2% nitric acid solutions. A standard reference material (SRM 1643-e) was used for the quality test, obtaining differences between the certificated and measured values between 2% and 10%.

3. Results and discussion

3.1. Red gypsum characteristics

Detailed information on the concentrations of major (determined by XRF) and trace (determined by ICP-MS) elements in the red gypsum generated at the factory in Huelva and also used in this work has been published elsewhere [7]. As expected, the main components of RG are CaO (33%) and SO_3 (27%), similar to those found in natural gypsum, although it also contains high proportions of TiO_2 (7.6%) and FeO_T (14%), and trace-level concentrations of metals such as Zn (225 ppm) and Cr (135 ppm). The granulometrics analysis of the RG show that 90% of the sample is finer than 60 μm, Fig. 1 and with a similar granulometric distribution to other wastes used in the manufacture of cement [5,8]. We can also state that the granulometry obtained is only slightly higher than the particle size for ordinary Portland cement, with 90% of the sample finer than 40 μm [14].

These similarities make RG a good potential substitute for natural gypsum, although the possible environmental impact of leaching pollutants from the cements manufactured with RG must be evaluated together with the more traditional mechanical, elastic and thermodynamic tests.

3.2. Comparative properties of the rg cements

The first stage following the formation of the three dried mixtures of clinker with RG, named YA, YB and YC, was to determine the appropriate water/cement (W/C) relation in weight terms in order to obtain a "normal" consistency in the paste formed, as defined by regulation UNE-EN 196-3. The optimum W/C ratios for the three different cements made with RG are shown in Table 1. This table also presents the optimum W/C ratio for the commercial cement used as a reference. The W/C ratios are quite similar, with no significant differences between the commercial and RG cements, and are comparable to those observed in other cements formed with gypsum-enriched waste [16].

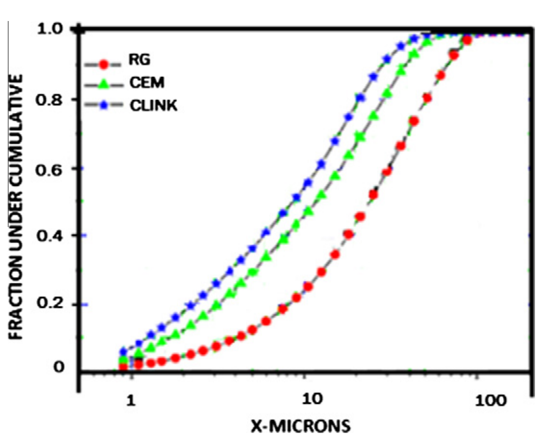

Fig. 1. Granulometric distribution of the conventional clinker (Clinker), commercial cement (CEM), and red gypsum (RG) used as raw materials in this work.

Table 1
Setting times established following a normalized protocol (UNE-EN 196-3) for the various cements formed by using different proportions of red gypsum. For comparison, see the setting times determined for the commercial cement taken as reference in this work. The optimum W/C ratios are also shown.

Sample	Optimum W/C	Initial setting time (min)	Final setting time (min)
Commercial cement (CEM)	0.266	139	224
YA (2.5% RG)	0.286	82	129
YB (5% RG)	0.272	108	298
YC (10% RG)	0.294	216	351

Table 1 also shows the setting times established in our laboratory for the three RG cements under analysis, as well as those for the commercial cement used as a reference. The setting times for the three RG cements are comparable to those obtained for the commercial cement.

To evaluate whether the setting times for the RG cements fulfill the requirements in regulation UNE-EN 196-3, Table 2 shows the minimum and maximum values stipulated for the setting times of cements with different resistances. The data show that the addition of RG in the proportions applied in this work produces setting times that fall within those required by the legislation, and it is noteworthy that the initial and final setting times are prolonged by increasing the proportion of RG used as an additive in cement fabrication, further underlining the role of RG as a retardant in the hardening of cement. Adding higher percentages of RG extends the initial and final setting times. For the YC cement (10% RG), the increase reaches 55.4% (from 139 to 216 min) and 56.7% (from 224 to 351 min) in the initial and final setting times, respectively, in relation to the commercial cement. Similar results have been obtained for other wastes with high gypsum content [8,10,16].

Table 3 shows the expansion values from the volumetric stability tests for the three RG cements, as well as for the commercial cement. The results indicate that the presence of RG in the cements formed does not significantly modify its expansion behaviour relative to the commercial cement, irrespective of the proportion of RG used as an additive. More importantly, the values comply with current legislation that indicates that the reference value for expansion obtained via the le Chatelier test for all cements should be less than 10 mm.

The resistances to flexion and compression calculated for the three RG cements analyzed in this work are shown in Fig. 2. Each result is the average of three tests performed on three different samples made from the same paste. The results for the commercial cement are also shown for comparison purposes.

Fig. 2 presents the results for compressive strength, showing that YA, YB and YC have 17.8, 23.1 and 31.5 MPa for 2 days, and 51.7, 57.9 and 59.6 MPa for 28 days, respectively. These results lead to the following conclusion: the mechanical behaviour of

Table 2
Minimum and maximum setting times permitted for cements of different resistance, according to Spanish legislation.

Cement resistance class	Setting times	
	Initial (min)	Final (min)
32.5 N	⩾75	⩽720
32.5 R		
42.5 N	⩾60	
42.5 R		
52.5 N	⩾45	
52.5 R		

Table 3
Expansions (mm) determined in the volumetric stability tests applied to three cements formed with red gypsum and to the commercial cement taken as reference. S1, S2, S3, S4, S5 and S6 are the six equal probes tested for each parameter measurement.

	Commercial cement (CEM)					
	S1	S2	S3	S4	S5	S6
Initial measurement	17	17	15	16	16	16
After 24 h	17	17	15	16	15	16
3 h–100 °C	15	15	16	–	–	–
7 days in water	–	–	–	17	15	16
Expansion (mm)	2	2	1	1	0	0
YA Sample (2.5% red gypsum)						
Initial measurement	18	18	17	17	17	18
After 24 h	20	21	19	20	19	21
3 h–100 °C	21	22	20	–	–	–
7 days in water	–	–	–	20	19	21
Expansion (mm)	1	1	1	0	0	0
YB Sample (5% red gypsum)						
Initial measurement	18	18	16	18	18	17
After 24 h	25	25	21	25	23	24
3 h–100 °C	25	26	22	–	–	–
7 days in water	–	–	–	25	23	24
Expansion (mm)	0	1	1	0	0	0
YC Sample (10% red gypsum)						
Initial measurement	18	17	18	17	16	16
After 24 h	23	22	23	20	21	20
3 h–100 °C	24	23	24	–	–	–
7 days in water	–	–	–	20	21	20
Expansion (mm)	1	1	1	0	0	0

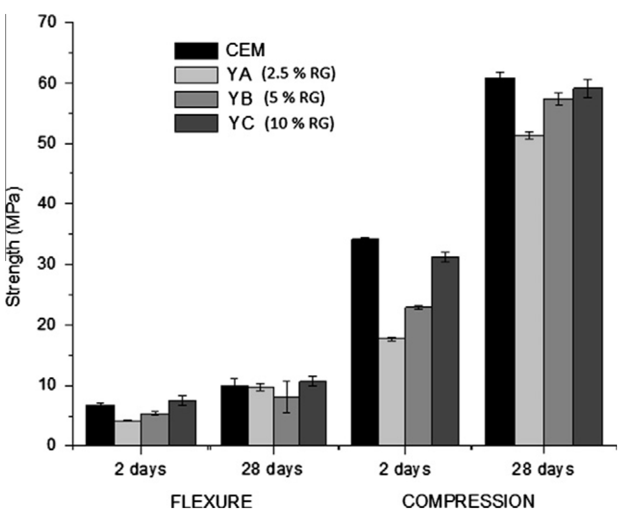

Fig. 2. Compressive and flexural strength behaviour of cement produced with RG and CEM (commercial cements).

the cements improves with the RG proportion, being the obtained resistance values very close to the commercial cement ones.

Similar behaviour was observed for flexural strength, with little difference in flexural and compressive strength values between YC (10% RG) and CEM. Our results also indicate that the behaviour of these mortars is similar to, or even better than, those obtained for the other wastes high in gypsum content currently used in cement manufacturing [16–18].

This fact is very relevant since it reinforces the benefits of adding RG to make cement by reducing the amount of clinker used, with all the financial benefits that this entails (cost savings). We should not forget that the reference commercial cement used in our study consists of approximately 97% clinker and 3% natural gypsum. Applying small RG proportions means that mechanical

Table 4
Values of compressive strengths (MPa) according to UNE-EN 196-1. R High initial strengths and N normal strengths.

Cement resistance class	Initial strength		Final strength	
	2 days	7 days	28 days	
32.5 N	–	⩾16.0	⩾32.5	⩽52.5
32.5 R	⩾10	–		
42.5 N	⩾10	–	⩾42.5	⩽62.5
42.5 R	⩾20	–		
52.5 N	⩾20	–	⩾52.5	–
52.5 R	⩾30	–		

resistance is only slightly lower than that for the commercial cement. Table 4 confirms that the mechanical resistance values for the three RG cements analyzed comply with current regulation (UNE-EN 196-1).

Linear retraction values were established in prismatic test samples (25.4 × 25.4 × 287 mm), and the results for the three RG cements and the commercial cement appear in Fig. 3. Here we observe how the major retractions occur during the first days of reaction. Then, as cement hydration times progress, the linear retractions diminish until they are almost constant in the final days.

The linear retraction behaviour of the cements made with red gypsum is similar to that for the commercial cement. As higher percentages of RG are added to the cement, lower retractions occur. All these linear retraction values are within the range permitted by current legislation, further increasing confidence in the viability of RG as a set retardant additive in cement fabrication.

Calorimetric analyses of the three RG cements were performed in order to determine the total heat released in their hydration processes, as well as the rate of heat released. During hydration, transitions occur from high to low energy states, the excess energy being released in the form of heat. Most commercial cements liberate 50% of their heat during the first 3 days of hydration. In addition, if the curve plotted for typical cement represents the liberation of heat versus time, we observe that a maximum peak of acceleration–deceleration occurs after about 6 h. This peak is associated to the formation and precipitation of C–S–H gel, the main product generated by cement hydration.

By applying the isothermal conduction calorimetric technique, we have determined the velocity of heat release, the time elapsed until the appearance of the acceleration peak, the total heat released associated to the peak and the total heat liberated after 60 h for the three RG cements and the commercial cement.

These values (Table 5) clearly indicate that the addition of RG diminishes the rate of heat release in the acceleration–deceleration

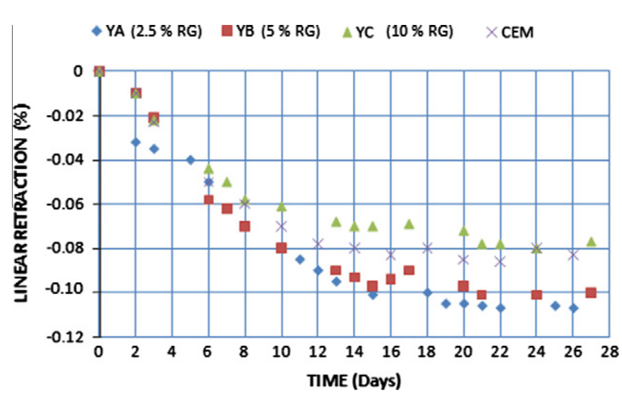

Fig. 3. Linear retraction curves obtained for CEM and the three cements formed with RG.

Table 5
Determinations performed in the calorimetric analysis of the three red gypsum samples analyzed in this work. For comparison, the determinations performed in the clinker used for the fabrication of the red gypsum cements, and in the commercial cement (CEM) taken as reference, are also shown.

Sample	Peak of acceleration–deceleration			Total heat after 60 h (kJ/kg)
	V (kJ/kg h)	t_V (h)	Q_V (kJ/kg)	
Cement	17.60	6.40	86.4	254.3
Clinker	12.50	7.20	71.4	258.3
YA	15.89	9.09	39.4	253.3
YB	14.30	11.30	96.68	231.0
YC	12.56	9.95	84.0	269.16

peak, down to 12.6 kJ/kg h in the YC sample, which is 28% lower than that obtained for the commercial cement. The addition of RG also retards the appearance of this peak until 9.95 h in the YC sample and 11.2 h in the YB sample. The total heat released in the cements formed with RG is fairly similar to that in the commercial cement, and is even slightly higher in the YC sample, but lower in the YB sample (231.0 kJ/kg). Adding RG delays the reaction and formation of the C–S–H gel which, in energy terms, is produced in a way that is very similar that of commercial cements.

3.3. Mobility of pollutants in RG cements

Table 6 shows the critical concentration values that define the ecotoxicity threshold of different metals; that is, if the concentration of a specific metal is lower than this threshold value for a given material, it will not have a significant impact when this material is released into the environment [21]. The data of the Table 6 indicate that the RG metal concentrations are below the ecotoxicity limits, and only the Cr concentration is slightly above this threshold, but due to the RG cement presents a RG concentration lower than 10%, the final Cr level will be very much lower than this threshold. The concentrations found in RG for the majority of the trace elements are similar or slightly higher than those typically found in soils, with the exception of Cd, which is 10 times higher.

It is also important to measure the chemical mobility (i.e. leachability) of the trace elements contained in the cement for an assessment its potential environmental impact. The TCLP test is widely used to determine hazardous waste potential. In this regard, some metals such as Cr (VI) can be readily released from the cement phase into the mixing water while the weathering of the hardened cement paste (i.e. hydration products such as CSH) under the influence of rain water, ground water or other factors such as biological activity which leads to the mobility of metals from the cement. Due to the high toxicity of hexavalent Cr, a European Directive [19] has been issued limiting the content of water-soluble Cr (VI) in cement to a maximum concentration of 2 mg/kg.

Table 6
Critical concentration values [19] and leachability of metals from the RG cements YC, RG samples and reference cement (CEM). (*) Average concentration of trace element concentration of the continental crust [20].

Concentration in solid samples (mg/kg)				Leaching TCLP test (μg/L)		
Element	Critical concentration	RG	(*)	RG	YC	CEM
As	20–50	10	4.8	1.8	1.9	1.1
Cd	3–8	1	0.09	<0.1	<0.1	<0.1
Co	25–50	16	17	65	<0.1	<0.1
Cr	75–100	109	92	103	82	89
Ni	100	30	47	176	4.1	3.3
Pb	100–400	19	17	8.0	8.3	2.9
Zn	70–400	212	67	–	–	–

Table 6 shows the lixiviation results for the YC (10% RG), the reference cement and RG samples. In all tests (for each sample analyzed), the Cr concentration in the leachate is lower than the 2 mg/kg, which is limit stipulated in the European Directive 2003/53/EC [21].

4. Conclusions

After a detailed analysis of the cements made for this study, and the performance of a wide range of physico-mechanical and chemical tests, the main conclusions regarding the possible use of RG in the fabrication of cements and mortars are the following:

(a) RG retards the setting times of the cements similar to natural gypsum. The addition of RG also diminishes the linear retraction of the cements fabricated.
(b) The mechanical resistances of the RG cements were equivalent to those obtained with natural gypsum.
(c) The TCLP test results infer that adding RG to the manufacturing of cement would not cause hazardous levels of leachable pollutants to enter the environment.

These conclusions lead us to deduce that RG can be a safe substitute for natural gypsum in the fabrication of commercial cements without decreasing the quality of the cements generated. In addition the best results, comparable to those for OPC (Ordinary Portland Cement) which contains 97% clinker and 3% natural gypsum were obtained when 10% of RG was mixed with the clinker. This means a saving on clinker of about 4–5%, while maintaining similar properties to those found in OPC. Therefore, a proportion of RG as high as 10% can be used in the manufacture of cements, while still complying with all quality requirements.

The availability and low cost of RG make it attractive as a raw material for cement production. Additional benefits include fewer waste management problems associated with disposal and pollution control, and the likely reduction in operating costs i.e. mining and raw material processing costs as natural gypsum.

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