Use of Carbonated Residual Brines as main component of filling grout

R. Delinière, Jean-Emmanuel Aubert, Bernard Husson

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R. Delinière[a], J.E. Aubert[a*], B. Husson[a]

[a] Université de Toulouse; UPS, INSA; LMDC (Laboratoire Matériaux et Durabilité des Constructions), 135 avenue de Rangueil, F-31 077 Toulouse cedex 4, France

Abstract

This study deals with the reuse of an industrial waste rich in $CaCO_3$ as a mineral addition and agent of stability in low-strength filling grout for soil reinforcement applications. The physical, chemical and mineralogical characteristics of these Carbonated Residual Brines (CRB) were determined and completed by a study of CRB behaviour in cement-based materials and of the optimization of a composition of low-strength filling grouts rich in CRB filling. The results showed that it was possible to use CRB in low-strength filling grout, in replacement of bentonite and fine sand, with better performance - especially in terms of stability.

Highlights

CRB is essentially composed of calcium carbonates (91%).

CRB can replace both bentonite and fine sand in low-strength filling grouts.

CRB strongly improves the stability of grouts.

Keywords: calcium carbonate; grout; flow; stability; filling; bentonite; CO_2 capture.

*Corresponding author. Tel. 0033 (0)5 61 55 66 97 Fax: 0033 (0)5 61 55 99 49;

e-mail: jean-emmanuel.aubert@univ-tlse3.fr

1. Introduction

Waste management is a major challenge for modern society. The amounts of waste produced each year continue to grow: world-wide production in 2006 was estimated at 3.4 to 4 billion tons of waste, half of which was industrial waste [1]. These wastes are mostly stored in landfills, posing significant problems (environmental, aesthetic and financial).

World production of sodium carbonate (Na_2CO_3) is estimated at 45 million tons per year, of which about 75% is produced by the Solvay process. This process, developed in 1861 by Ernest Solvay, produces Na_2CO_3 from sodium chloride and calcium carbonate according to the following equation: $2NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2$ (see details of the Solvay process in Figure 1). Ammonia also occurs in the process but it is not considered as a secondary raw material because it is totally regenerated and recycled in the process. This process generates large amounts of waste, essentially in the form of alkaline brines that have so far been stored in desludging tanks or directly discharged into the sea or rivers near industrial sites. Today, the storage of these residues in desludging tanks is becoming impossible because of the large areas immobilized by this storage in the past hundred years or so. Moreover, for obvious environmental reasons, the discharging of such residues in seas or in rivers is not sustainable and replacement solutions must be found.

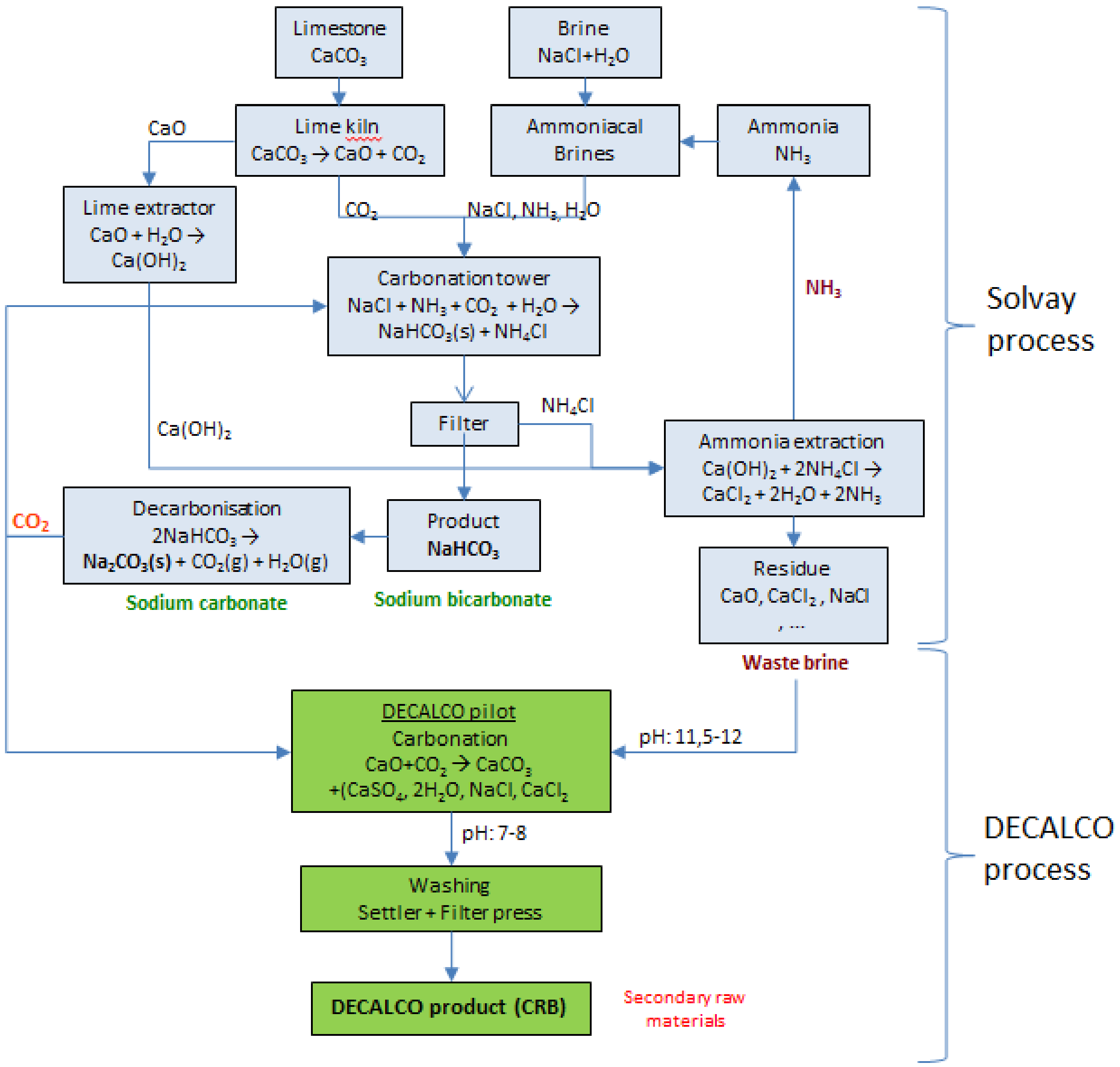

Figure 1: Chemical reactions of the Solvay process and of the DECALCO process.

The current context, with a rarefaction of natural resources, is in favour of alternative waste recycling solutions that produce new materials, especially in the field of road and construction materials. In this context, the project DECALCO was developed to reduce the impact of the Solvay process for the production of sodium carbonate. The method treats the waste brines using CO_2 recovered from the industrial plant, which leads to the production of lime carbonates called Carbonated Residual Brines (CRB) [2]. This method makes it possible to reduce the environmental impact by transforming waste from the production of Na_2CO_3 into an inert and recoverable by-product while reducing the CO_2 emissions of the industrial plant. The CRB obtained using this process are in the form of a limestone filler, for which several uses in the field of civil engineering materials can be considered, including that of filling grout, which is the subject of the study presented in this article.

A grout is a stable suspension usually composed of a hydraulic binder (cement, hydraulic lime or air lime and pozzolan) and water. Depending on the applications, the mechanical properties and the rheological behaviour of grouts can be modified by the addition of substances such as mineral fillers (sand, filler or other mineral additions), an agent of stability (clay, polymer), admixtures (superplasticizer) or fibres [3-5]. There are several types of grout, which are used in various ways according to their compositions and their performances, in particular their mechanical strength. For example, some lime-based grouts are used to consolidate masonry by injection. For such applications, the mechanical strength of the grout can be enhanced by the addition of silica fume, coal fly ash and superplasticizer [6-9] but the compressive strength remains low (5 to 10 MPa) [10]. In contrast, it is possible to obtain cement-based grout, used for concrete repair, that reaches a compressive strength ranging between 95 and 110 MPa [11]. Some grouts are also used for the storage of radioactive waste [12-14], in which case their compressive strengths range from 10 to 70 MPa [15]. Grout can be used for heat exchanges in geothermal applications, where fly ash, bentonite or superplasticizer [16, 17] are employed to improve the strength of the material, which then ranges from 32 to 41 MPa [18]. Some cement-based grouts are used in mining and geotechnical engineering for grouted rock bolts, providing ground anchorage, and for soil nailing, used to treat unstable natural soil slopes or to stabilize retaining walls or existing fill slopes (embankments). In such cases, the grouts have a high cement content and the compressive strength of these materials is thus significant (from 17 to 82 MPa [19-21]).

Finally, low-strength filling grouts are used for soil reinforcement (improving soil stability during the construction of a tunnel, improving soil bearing capacity, etc.), for filling underground cavities (mining, quarries, etc.) and consolidating soils under foundations. The grout used in these cases should have low viscosity and a grain size sufficiently small to allow the grouts to flow into the cracks but high compressive strength is not required (1.5 MPa) [22, 23]. The volumes concerned by this type of use are significant and in accordance with the need to find solutions for using the large volume of residue produced each year by the production of Na_2CO_3.

The objective of the work presented here was to develop low-strength filling grouts containing the highest possible amount of Carbonated Residual Brines (CRB). The physical, chemical and mineralogical characteristics of CRB are presented first. CRB could be considered as mineral additions and it is conventional to characterize this type of materials using tests carried out on cement-based pastes and mortars (consistency, setting time and activity index) as presented in the second part of the paper. The specific properties of grouts (flowability and stability) are then studied because the characteristics of grouts and cement pastes can differ considerably even though their raw materials are similar but used in different proportions. This study leads to the optimization of a composition of low-strength filling grouts rich in CRB that meet the specifications imposed for this type of grout.

2. Materials and procedures

2.1 Materials

2.1.1 Raw materials

Carbonated Residual Brines (CRB)

The CRB studied in this paper came from the industrial site of Torrelavega, Spain. This material was prepared in an industrial pilot equipped with a vertical carbonation column able to treat the brines coming from the industrial production of Na_2CO_3 with a flow of 1.1 m^3/h. The brines were introduced into the upper part of the column, while a mixture of CO_2, air and water was injected into the lower part [24]. A similar process was used for the carbonation of MSWI fly ash in another work [25]. After this wet carbonation, the product was dried using a filter press and took the form of sheets of agglomerated particles. The cohesion of these particles was relatively high and it was necessary to crush the material to transform it into a powder usable for mortar or grout preparations. A preliminary study showed that the use of CRB crushed to a powder would lead to a problem of water demand because of the residual porosity of the small aggregates. It was thus preferred to use CRB mixed with water in the form of a suspension. CRB-suspension was prepared by mixing CRB and water in a turbo mixer with a 65-mm-diameter head (the same equipment that was used for mixing the grouts) with a water/CRB ratio equal to 1.

Binders

Two types of binder were used in this study: an ordinary Portland cement (OPC) containing more than 95% of cement clinker (CEM I 52.5R), and a binary blend cement having a high Ground Granulated Blast Furnace Slag (GGBFS) content, ranging between 81 and 95% (CEM III/C 32.5 N PM-ES). CEM I was used to evaluate the reactivity of the CRB in accordance with EN 196-1 by measuring their activity index. However, because of their origin, it is probable that CRB contained sulfates and thus, for practical applications (low-strength filling grouts in the present case), it was preferable to use sulfate resistant cement such as CEM III/C.

Sands

Two types of sand were used in this study. Firstly, a standard siliceous sand was used to make the standardized mortars. The particle size of this sand was too coarse for use in grout and another type of sand (0-0.315 μm) was used to make the grouts. This was a siliceous sand composed of 95% quartz. The size distribution of the two sands is presented in Fig. 2.

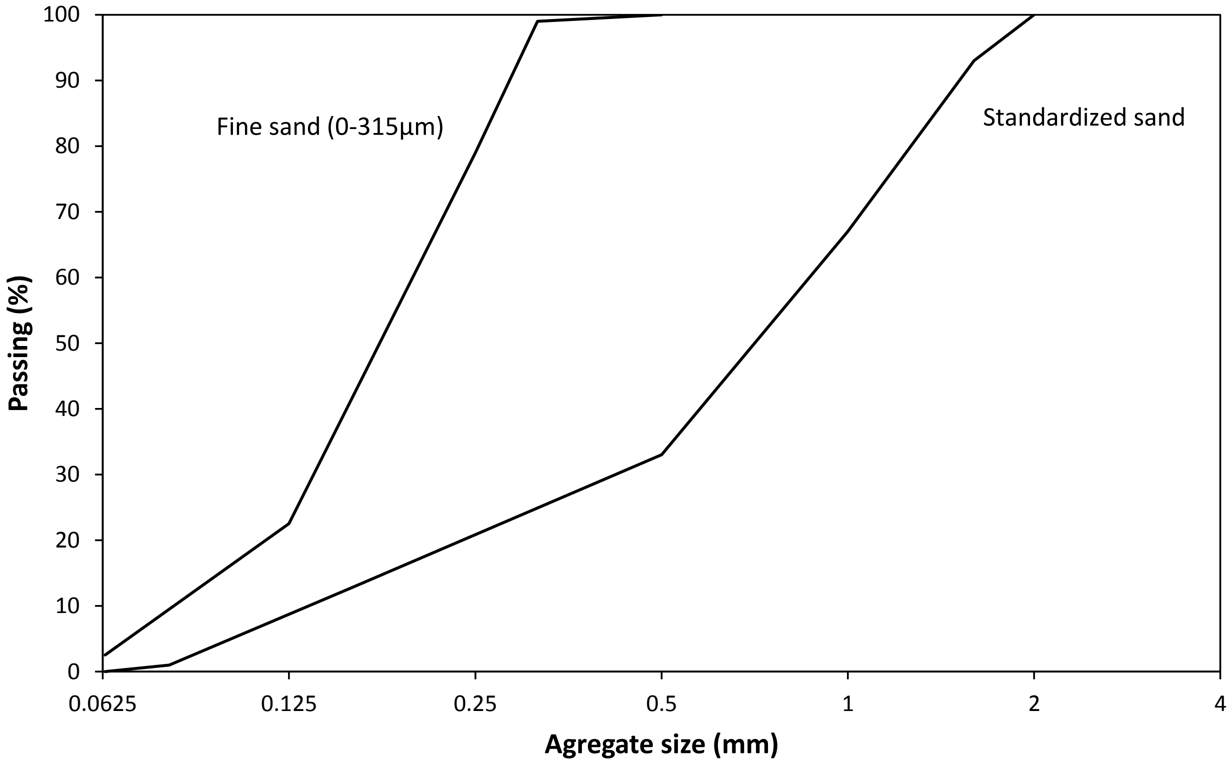

Figure 2: Size distribution of the sands used

Bentonite

Bentonite is colloidal clay that swells significantly in contact with water (original volume multiplied by 3 to 18 [26]). It is generally used in small quantities in grouts to increase their stability. The addition of bentonite to grouts allows the formation of a homogeneous colloidal mixture that reduces the sedimentation of the fresh grout during its use but this addition often leads to an increase in the setting time of the mixtures and a decrease in their compressive strength [27, 28].

The bentonite used in this study was a sodic bentonite CV 15 coming from the company Süd-Chemie based in Munich. It was essentially composed of Montmorillonite.

2.1.2 Compositions of cement pastes and mortars

Pastes were formulated with cement and CRB and used for setting time measurements while mortars composed of cement, CRB and coarse sand were used for activity index determination. CRB was introduced into cement pastes and mortars to replace part of the cement. Two compositions were studied: a reference cement paste (or mortar) (100% cement) and a CRB-containing paste (75% cement and 25% CRB). In the rest of the paper, the term "binder" will be used to mean the cement or the cement and CRB mixtures.

For cement pastes, sufficient amounts of water were added to obtain a normal consistency in accordance with the standardized European EN 196-3 test method [29]. For the mortars, the sand/binder and water/binder ratios were equal to 3 and 2 respectively.

2.1.3 Grout compositions

The low-strength filling grouts had to meet three specifications [23, 30-32]:

- the flow time, measured 1 min after the end of mixing by Marsh cone with a nozzle diameter of 8 mm, had to be less than 15 seconds,
- the stability of the grouts was evaluated using a decantation test: the decantation of the fresh grouts had to be lower than 5% after three hours,
- the compressive strength at 28 days had to be higher than 1.5 MPa.

In a previous work [32], Trinh optimized a low-strength filling grout composition using CEM III, water, sand (0-0.315µm) and bentonite. Some tests were carried out to determine the most efficient composition, the objective being to use the highest acceptable amount of CRB in grout and to replace both sand (0-0.315µm) and bentonite if possible. Three types of mixtures were tested:

- a reference mixture containing cement, sand and bentonite,
- mixtures containing 50 wt.% and 100 wt.% of CRB in replacement of fine sand and bentonite.

For these mixtures, the effect of water content on the grout characteristics was examined by varying the W/C ratio.

The grout compositions tested are shown in Table 1. The quantities given in the Table 1 are those used to prepare three 4x4x16 cm^3 samples. The compositions are designated by two numbers, the first referring to the percentage of sand replacement by CRB and the second corresponding to the W/C ratio. In Table 1, the characteristics of fresh and hardened grouts are also presented but these results will be discussed in Section 3.3.

Table 1: Compositions and characteristics of grouts

Raw materials (g)					W/C	Ref.	Stability (%)	Flow time (s)	fc_{28} (MPa)
CEM III/C	CRB	Sand	Bentonite	Water			<5%	<15s	>1.5MPa
140	0	754	16	441	3.15	0-3.1	5	**13**	**1.6**
140	0	754	16	490	3.50	0-3.5	8	**12**	**1.6**
140	0	754	16	539	3.85	0-3.9	11	**12**	1.3
140	385	385	0	623	4.45	50-4.5	**0**	**14**	**2.0**
140	385	385	0	683	4.88	50-4.9	**1**	**12**	**1.8**
140	385	385	0	742	5.30	50-5.3	**2**	**11**	1.4
140	770	0	0	735	5.25	100-5.3	**1**	71	**2.8**
140	770	0	0	805	5.75	100-5.8	**0**	24	**2.2**
140	770	0	0	875	6.25	100-6.3	**0**	18	**2.0**
140	770	0	0	910	6.50	100-6.5	**0**	**15**	**2.0**
140	770	0	0	945	6.75	100-6.8	**0**	**13**	**1.9**

2.2 Procedures

2.2.1 Chemical, mineralogical and physical characterization

The major oxides composition of CRB was estimated on the basis of the macroelemental analysis carried out on digested samples by Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) (Thermo Fischer ICap 6500). The chloride (Cl) and sulfate (SO_3) contents were measured by ionic chromatography (Dionex ICS 30) after acidic dissolution.

The crystalline phases were identified on a crushed sample using a Siemens D5000 powder X-ray diffractometer equipped with a monochromator using a Kα (λ = 1.789 Å) cobalt anticathode.

The size distribution of CRB in the form of a suspension was analysed using a laser particle size analyser (CILAS 1090 LD) and its specific surface area was measured using a BET apparatus (Flowsorb II 2300 (Micromeritics)). A scanning electron microscope (JEOL JSM-6380LV) was used to study the morphology of the particles of CRB. These observations were carried out on metallized powder stuck to an adhesive tape.

2.2.2 Preparation and characterization of cement pastes and mortars

The pastes were mixed and the setting time was measured according to the European standard test method EN 196-3 [29].

The fluidity of fresh mortars was determined according to standard P 15-437 [33]. This method involves measuring the time taken by a cement mortar to flow from the large compartment of a workability measuring device and reach a fixed horizontal reference line cut into the wall of a second compartment, when subjected to vibration. The 4x4x16 cm^3 mortar prisms were cast in steel moulds, demoulded after 1 day and then cured at 20°C under water according to the European standard test method EN 196-1 [34].

2.2.3 Preparation and characterization of grouts

Before testing, CRB were deagglomerated in water using a turbo mixer with a 65 mm-diameter head for 15 min at a controlled speed of 4000 rpm. The bentonite was also premixed in water. Then suspensions were mixed with cement and sand (if necessary), using an automatic mixer for normalized mortar and paste for 5 min. The flow time was measured 1 min after the end of mixing by Marsh cone (nozzle diameter 8 mm) according to standard NF P 18-358 [35]. The stability of the grouts was evaluated using a decantation test (NF P 18-359) starting 4 min after mixing [36]. The test measured the ratio of the water volume collected after 3 h at the top of a test tube filled with grout relative to the total initial volume. Compressive strength tests were performed at 28 days on prismatic specimens of dimensions 4x4x16 cm^3 according to standard EN 196-1. The hardening of the grouts being very slow, the grouts were kept in their polystyrene moulds and stored at 95% RH and 20°C for 28 days.

3. Results and discussion

3.1 Chemical, mineralogical and physical characterization of CRB

The chemical compositions of the materials used in this study are presented in Table 2 and the XRD pattern of CRB is presented in Figure 3.

Table 2: Chemical compositions of raw materials (wt.%)

	SiO_2	CaO	MgO	Al_2O_3	Fe_2O_3	K_2O	Na_2O	SO_3	Cl	LOI
CEM I	20.2	64.2	1.0	4.7	2.4	0.2	0.1	3.5	< 0.1	3.1
CEM III/C	32.3	43.9	6.3	10.5	0.8	0.6	0.5	2.3	< 0.1	3.1
CRB	1.4	51.5	1.0	0.4	0.3	<0.1	0.6	2.6	0.9	43.0

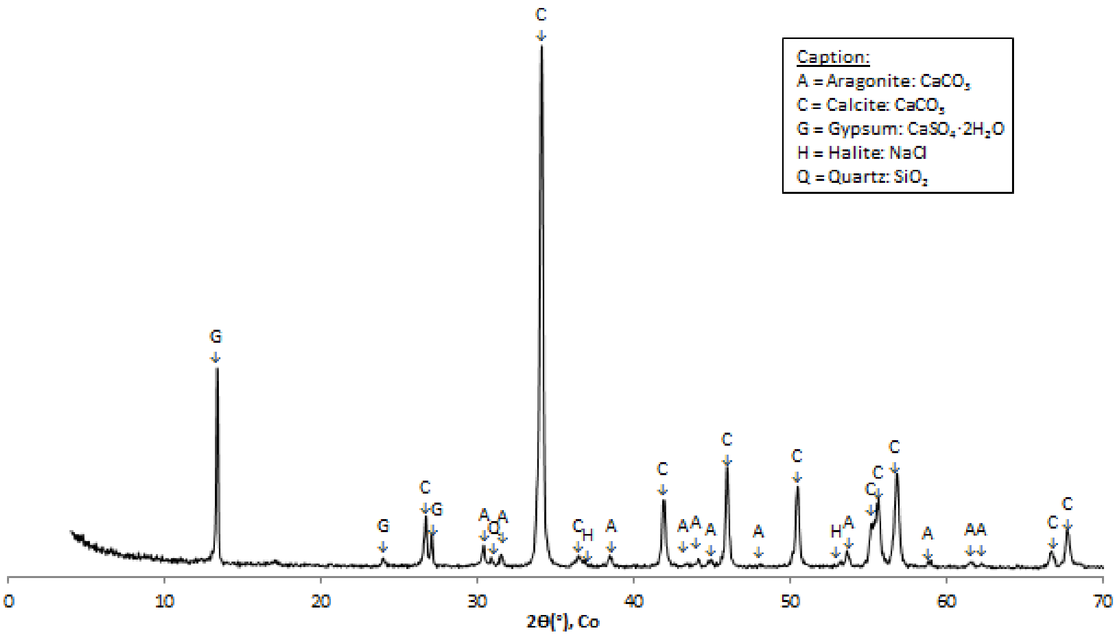

Figure 3: XRD pattern of CRB

Both the chemical composition and XRD pattern confirmed that CRB was essentially composed of calcium carbonates ($CaCO_3$) in the forms of calcite and aragonite. The chemical composition highlighted a significant amount of residual sulfates (2.6%) and chlorides (0.9%). The presence of these two elements is worrying for the potential use of CRB in cement-based materials: sulfates imply a significant risk of expansion due to delayed ettringite formation and chlorides are not compatible with the use of CRB in reinforced materials due to the risk of corrosion of the steel bars. The use of a sulfate resistant cement such as CEM III/C for this study would solve the problem of the high sulfate content and the choice of CRB for low-strength filling grouts that do not contain steel bars would be consistent with the chloride content of CRB. XRD analysis showed that sulfates were in the form of gypsum ($CaSO_4$, $2H_2O$) and chlorides in the form of halite (NaCl). Finally, the chemical composition showed the presence of SiO_2 (1%) corresponding to the low quartz content identified by XRD. There was also a small amount of MgO that could be present in substitution of CaO in the calcium carbonates. Both chemical and XRD analyses allowed a mineralogical composition of CRB to be calculated: calcium carbonates (91%), gypsum (6%), halite (1%) and quartz (1%).

The physical characteristics of CRB are presented in Table 3.

Table 3: Physical characteristics of CRB

Particle size distribution (µm)	
D_{10}	1.1
D_{50}	5.7
D_{90}	22.7
BET surface area (m²/g)	9.94

The results of laser particle size analysis showed that CRB was very fine, its average size (D50) being close to 6 µm. This is in accordance with the size distribution of calcareous filler reported in the literature, which ranges from 1 to 60 µm [37]. This great fineness was confirmed by the measurement of the specific surface area, which was close to 10 m²/g whereas that of conventional calcareous filler is much lower (from 1.2 m²/g to 7 cm²/g [38, 39]).

The morphology and size of the minerals were studied by Scanning Electron Microscopy (SEM). Some examples of the observations are presented in Figure 4. The figure shows two grains (calcite and gypsum) with dimensions close to 10 µm that are surrounded with small particles (less than 1 µm) of precipitated calcium carbonates. SEM observations show that CRB seem to be finer than suggested by the laser particle size analyser measurements as a significant proportion of particles were smaller than 1 µm.

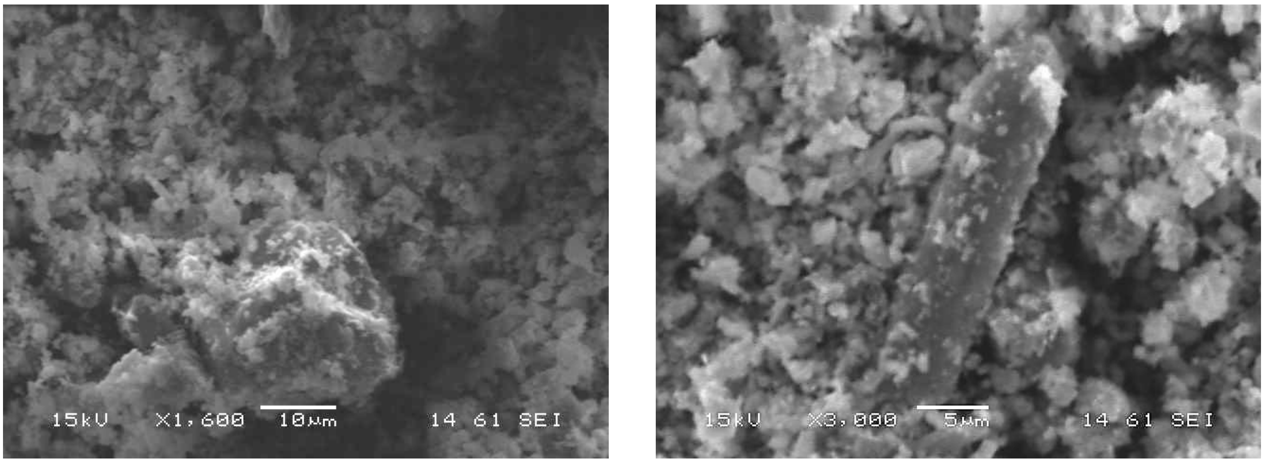

Figure 4: Scanning electron micrograph of CRB: grain of calcite (left) or gypsum (right) surrounded by precipitated calcium carbonates

3.2 Behaviour of CRB in cement pastes and mortars

The Water/Binder ratios necessary to obtain a standardized consistency and setting time for the cement pastes are presented in Table 4. These measurements were carried out on mixtures containing the two types of cement: CEM I used for the measurement of the activity index of CRB and CEM III used for the manufacture of the low-strength filling grouts.

Table 4: Water demand and setting time of CRB-containing cement pastes

Composition	Water/Binder ratio	Setting time (h)
100 wt.% CEM I	0.30	2.33
75 wt.% CEM I + 25 wt.% CRB	0.33	2.00
100 wt.% CEM III/C	0.33	4.00
75 wt.% CEM III/C + 25 wt.% CRB	0.34	4.50

The results in Table 4 show that the substitution of 25 wt.% of cement by CRB in the form of suspension had practically no effect on the Water/Binder ratio (only a slight increase could be observed for both cements). The same conclusion can be drawn for the effect of CRB on the setting time: only slight variations in setting time were observed for both cements, which should not pose a problem for the potential reuse of CRB in cement-based materials.

The workability and the compressive strength of CRB-containing mortars are presented in Table 5. As specified in the European standard on cement [34], only CEM I was used for this part of the study to determine the activity index of CRB.

Table 5: Workability and compressive strength of CRB-containing mortars

Composition	Flow time (s)	Compressive strength (MPa)			Activity Index (28d)
		2d	7d	28d	
100% CEM I	2±1	35±1	54±1	70±2	
75% CEM I + 25% CRB	5±1	30±1	44±1	51±2	0.73

The results in Table 5 confirm those of Table 4 concerning the effect of the substitution of 25 wt.% cement by CRB on the workability of cement-based materials: use of CRB in the form of a suspension in mortars induced a slight decrease of workability but this was so limited that it does not call into question the reuse of CRB in cement-based material, especially as a main component of low-strength filling grout. Concerning the effect on compressive strength, the ratio between the compressive strength of standard mortar specimens prepared with 75 wt.% test cement plus 25 wt.% CRB by mass and the compressive strength of standard mortar specimens prepared with 100 wt.% test cement permitted the activity index of CRB to be calculated. The activity index was equal to 0.73, which is very close to the standard activity index for conventional calcareous filler (0.71) [40]. This result shows that CRB could be considered as conventional calcareous filler from the mechanical point of view and is encouraging for its use as a main component of filling grouts.

3.3 Fresh and hardened characteristics of CRB-containing grouts

Table 1 presents the fresh (stability and flow time) and hardened (28d compressive strength) characteristics of grouts. The minimal specifications of these characteristics that low-strength filling grouts have to meet are recalled in the table [23, 30-32]. Table 1 shows the combined effects of water and CRB additions on the fresh and hardened characteristics of grouts. The three characteristics change in opposite directions: for example, for the reference mixture (0% of CRB), an increase in W/C ratio improves the fluidity of mixtures but, at the same time, increases the decantation and decreases the compression strength. The specifications were met for mixture "0-3.1", without CRB.

The addition of CRB strongly improved the stability of fresh grouts since, whatever the W/C ratio, the stability criterion was satisfied for all mixtures (the decantation was close to 0% for all mixtures containing CRB). This is a major result since the use of CRB in grout avoids the addition of bentonite as a stability agent. However, replacement of sand by CRB also led to a significant increase in the W/C ratio needed to meet the flow test criterion. This effect had already been observed during the study of cement pastes and mortars but, in the case of grouts, the increase was more significant as W/C increased from 3.85 for the reference mixture (0% CRB) to 4.45 for mixtures with 50 wt.% of CRB and 6.75 for those with 100 wt.% of CRB. Nevertheless, it is interesting to note that this increase in W/C did not lead to a strong decrease in the compressive strength at 28 days. For mixtures with 50 wt.% and 100 wt.% of CRB, the strength at 28 days was sufficient at all W/C ratios (except the "50-5.3" mixture, for which the increase of the W/C to 5.3 was not necessary because the specifications of fluidity were already met for the mixture having a W/C ratio of 4.9).

From an economic and environmental point of view, it is obviously better to use the maximum acceptable amount of CRB in the grout. Figure 5 sums up the results obtained for mixtures containing 100 wt.% of CRB.

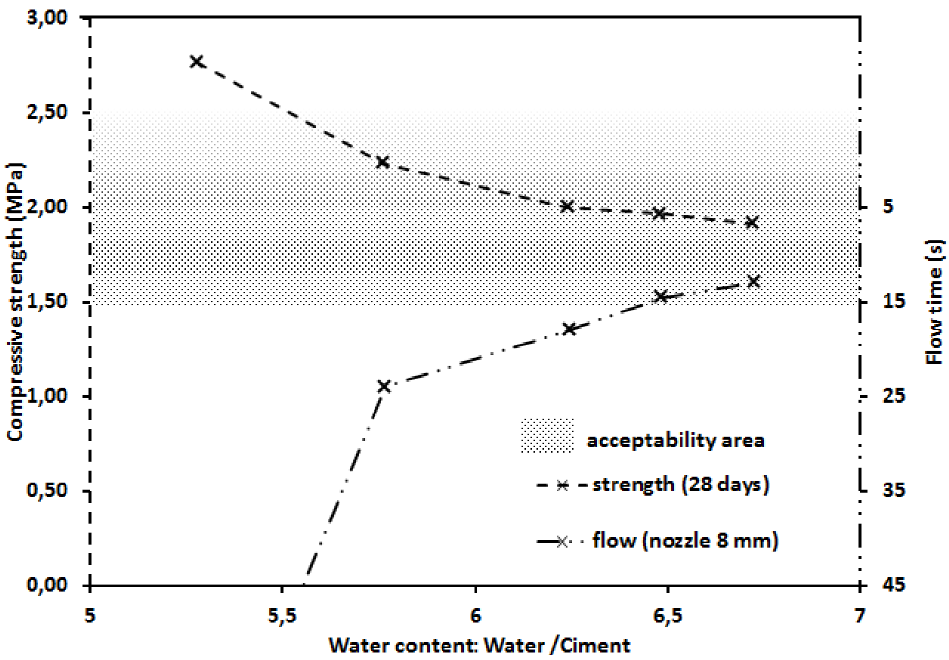

Figure 5: Fresh and hardened characteristics of low-strength filling grouts containing 100 wt.% of CRB

Figure 5 shows that the specification for compressive strength was reached for all mixtures even if the compressive strength decreased when the W/C ratio increased. The stability of the mixtures containing 100 wt.% of CRB was always excellent. Thus, to meet the requirements, it was only necessary to increase the W/C ratio until the required flow time was achieved (W/C equal to 6.5). Moreover, it is interesting to note that the low-strength filling grouts containing 100 wt.% of CRB performed better in the fresh and hardened states than the reference grouts containing fine sand and bentonite, particularly with regard to their stability and compressive strength. It would thus be possible, in a further optimization study, to reduce the amount of cement contained in the grouts rich in CRB to reach the limit of 1.5 MPa at 28 days and thus to make the CRB-containing mixtures even more competitive from the economic point of view.

4. Conclusion

This study has dealt with the reuse of Carbonated Residual Brines as a mineral addition and agent of stability in low-strength filling grout for soil reinforcement applications.

The chemical and mineralogical characterization of this residue showed that it was essentially composed of calcium carbonates (91%) but contained significant amounts of sulfates (2.6%) and also chlorides (0.9%), which could be worrying for its reuse in reinforced cement-based materials due to problems of delayed ettringite (sulfates) and corrosion (chlorides). Nevertheless, for the application considered (low-strength filling grouts), this would not be a problem, on condition that a low-C3A cement was used as was done in this study (CEM III/C). The physical characterization of CRB highlighted the marked fineness of this precipitated carbonate (D50 equal to 5.7 µm).

The study on cement pastes and mortars revealed that the use of CRB did not lead to significant modifications of the setting time or workability of cement-based materials. Moreover, the result of compressive strength measured on mortars showed that CRB could be considered as a conventional calcareous filler from the mechanical point of view.

The results obtained on low-strength filling grouts showed that CRB could advantageously replace the fine sand and bentonite contained in conventional grouts. CRB could thus be an interesting substitute for more expensive products and the results showed that the performance levels achieved with the CRB-containing grouts were even better than those of the reference grout. The fact that CRB has a very strong stabilizing effect certainly constitutes one of main findings of this study and could be useful in industrial applications other than civil engineering. In addition, the reuse of CRB would be interesting from an environmental standpoint for at least two main reasons: firstly, the reuse of an industrial waste in replacement of conventional materials would help to save natural resources and, secondly, the process that forms CRB reduces the CO_2 emissions of the industrial plant. However the sulfate and chloride contents limit the possible fields of reuse of CRB in civil engineering and it could be interesting to add an industrial washing step into the process to reduce the amounts of these two soluble elements and thus to develop new potential applications. In particular, the study showed that CRB had exceptional properties as an agent of stability, which may be useful in the production of self-compacting concrete, for example.

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