



## Use of Carbonated Residual Brines as main component of filling grout



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### 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.

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### ABSTRACT

This study deals with the reuse of an industrial waste rich in CaCO<sub>3</sub> 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 behavior 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.

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## 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 3.4–4 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<sub>2</sub>CO<sub>3</sub>) 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<sub>2</sub>CO<sub>3</sub> from sodium chloride and calcium carbonate according to the following equation:  $2\text{NaCl} + \text{CaCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{CaCl}_2$  (see details of the Solvay process in Fig. 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.

The current context, with a rarefaction of natural resources, is in favor 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<sub>2</sub> 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<sub>2</sub>CO<sub>3</sub> into an inert and recoverable by-product while reducing the CO<sub>2</sub> 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

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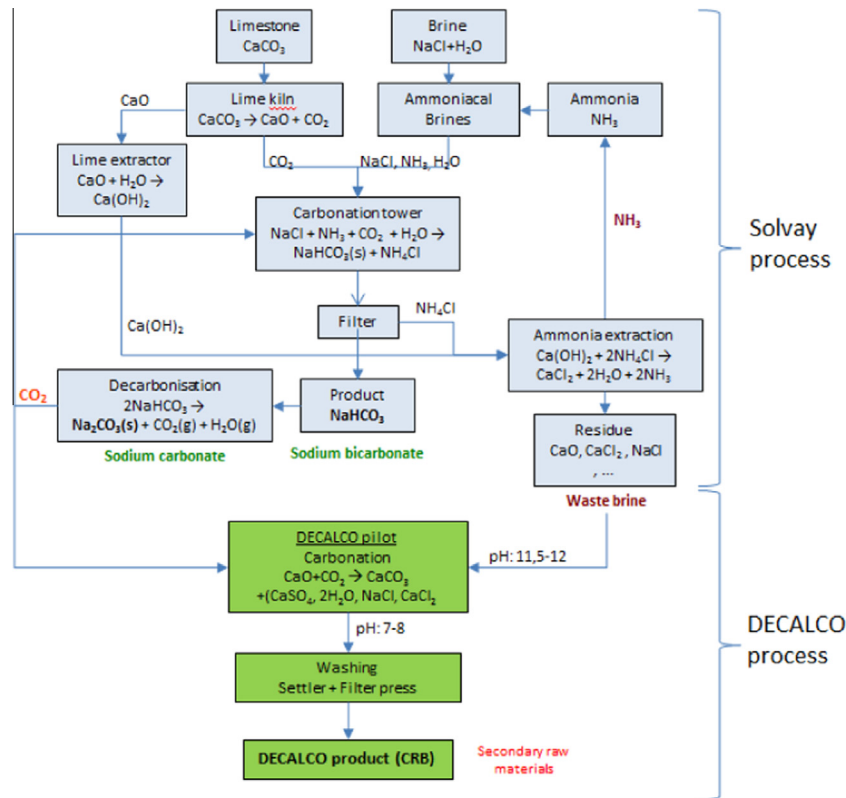


Fig. 1. Chemical reactions of the Solvay process and of the DECALCO process.

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 behavior 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 fibers [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 (5–10 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<sub>2</sub>CO<sub>3</sub>.

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

2.1.1.1. 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<sub>2</sub>CO<sub>3</sub> with a flow of 1.1 m<sup>3</sup>/h. The brines were introduced into the upper part of the column, while a mixture of CO<sub>2</sub>, air and water was injected into the lower part [24]. A similar process was used for the carbonation

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