

This item was submitted to [Loughborough's Research Repository](#) by the author.  
Items in Figshare are protected by copyright, with all rights reserved, unless otherwise indicated.

## **A methodologic approach based on hydrocyclone separation and acid leaching to purify gypsum from refurbishment plasterboard waste**

PLEASE CITE THE PUBLISHED VERSION

<https://www.sardiniasymposium.it/en/symposium-proceedings>

PUBLISHER

CISA

VERSION

AM (Accepted Manuscript)

PUBLISHER STATEMENT

Reproduced with permission of the publisher

LICENCE

CC BY-NC-ND 4.0

REPOSITORY RECORD

Castro-Díaz, Miguel, Mohamed Osmani, Sergio Pialarissi-Cavalaro, Paul Needham, Jeremy Thompson, Sam Elliott, Bill Parker, and Tatiana Lovato. 2021. "A Methodologic Approach Based on Hydrocyclone Separation and Acid Leaching to Purify Gypsum from Refurbishment Plasterboard Waste". Loughborough University. <https://hdl.handle.net/2134/15015081.v1>.

# A METHODOLOGIC APPROACH BASED ON HYDROCYCLONE SEPARATION AND ACID LEACHING TO PURIFY GYPSUM FROM REFURBISHMENT PLASTERBOARD WASTE

Miguel Castro-Díaz <sup>1</sup>, Mohamed Osmani <sup>1</sup>, Sergio Cavalaro <sup>1</sup>, Paul Needham <sup>2</sup>, Jeremy Thompson <sup>2</sup>, Sam Elliott <sup>2</sup>, Bill Parker <sup>3</sup>, Tatiana Lovato <sup>3</sup> and David Jalland <sup>3</sup>

<sup>1</sup> School of Architecture, Building and Civil Engineering, Loughborough University, Loughborough, Leicestershire LE11 3TU, United Kingdom

<sup>2</sup> ENVA, Enviro Building, Private Road 4, Colwick Industrial Estate, Nottingham, Nottinghamshire, NG4 2JT, United Kingdom

<sup>3</sup> British Gypsum, East Leake, Loughborough, Leicestershire, LE12 6JT, United Kingdom

**ABSTRACT:** One of the main challenges in recycling gypsum from refurbishment plasterboard waste for the production of new plasterboards comes from the difficulty to achieve consistent purity values higher than 92 wt% via current treatment technologies. These treatments generally rely solely on magnetic and manual physical separation combined with grinding. Although gypsum purity values ranging from 75 wt% to 90 wt% can be achieved, this depends mainly on the quality of the refurbishment plasterboard waste received, as current treatments have limited efficiency and customisation possibilities. As a result, the highest practical rate of recycled gypsum in new plasterboards is currently around 20 wt%. Therefore, physical and chemical treatments have the potential to increase the content of recycled gypsum in new plasterboards. As part of the ICEBERG project from the European Union's Horizon 2020 Research and Innovation Framework Programme under grant agreement No. 869336, hydrocyclone separation and acid purification have been evaluated in this work to achieve purity values above 96 wt% in gypsum from refurbishment plasterboard waste. The plasterboards were crushed and sieved to obtain gypsum particles less than 250  $\mu\text{m}$  in size. For hydrocyclone separation testing, a centrifugal pump was used to produce a gypsum slurry in a mixing tank and to feed the slurry to a commercial mini-hydrocyclone of 2 inches in diameter. Acid leaching was performed at atmospheric pressure on the initial waste gypsum and on a sample collected at the hydrocyclone, using different temperatures, residence times and sulphuric acid solutions. The purity of gypsum obtained from individual and sequential hydrocyclone separation and acid leaching tests was determined through X-ray fluorescence. Furthermore, the calcination behaviour dihydrate phase content of the sample with the highest purity was determined through thermal gravimetric analysis. Hydrocyclone separation was not effective for gypsum purification but acid leaching at 90 °C for 1 hour using a 5 wt%  $\text{H}_2\text{SO}_4$  solution produced recycled gypsum with more than 96 wt% chemical purity and dihydrate content.

**Keywords:** refurbishment plasterboard waste gypsum recycling hydrocyclone acid leaching

## 1. INTRODUCTION

Plasterboard used in construction usually contains natural gypsum, synthetic gypsum, paper, fibres, resins and paints. Natural gypsum rock is a non-inert material predominantly made of calcium sulphate dihydrate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) that has a neutral pH and a humidity of 8-10 wt%. It may also contain other minerals such as calcite ( $\text{CaCO}_3$ ), dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ), silica ( $\text{SiO}_2$ ) and various types of clay. The synthetic gypsum used in plasterboard manufacturing is commonly obtained at flue gas desulphurisation (FGD) plants from coal-fired power stations. The FGD is identical to natural gypsum from a chemical and crystallographic point of view, but contains impurities derived from the manufacturing process (Kuntze, 2009; Lushnikova and Dvorkin, 2016).

However, most gypsum from plasterboard waste ends up in landfills, where they can decompose contributing to the generation of toxic hydrogen sulphide ( $\text{H}_2\text{S}$ ). Gypsum is a material that can be recycled indefinitely at a cost that is lower than that of landfill disposal (Jiménez-Rivero and García-Navarro, 2016). The standard end-of-life plasterboard recycling process involves several steps aimed at removing impurities, namely manual segregation, grinding, sieving, and ferrous and non-ferrous magnetic separation. These are followed by calcination in a rotary kiln to convert  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  to calcium sulphate hemihydrate ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ). Finally,  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  is rehydrated to produce gypsum crystals that bind strongly. Recycled gypsum intended for plasterboard manufacturing must meet several technical requirements. The European Union, through the Life+ GtoG project, established a minimum purity in terms of dihydrate phase content of 80 wt% (Jiménez-Rivero and García-Navarro, 2017). This minimum dihydrate content compares with that recommended by the Eurogypsum Recycling Working Group of at least 85 wt%, or more than 85 wt% recommended in the British standard document BSI PAS 109 (GtoG-DC2 report, 2016; BSI PAS 109, 2013).

One of the main challenges to obtain recycled gypsum from refurbishment plasterboard waste that is suitable for the production of new plasterboards comes from the difficulty to achieve consistent calcium sulphate dihydrate content values higher than 92 wt% via current treatment technologies (Jiménez-Rivero, A., García-Navarro, J., 2017). Although gypsum purity ranging from 75 wt% to 90 wt% can be achieved (GtoG-DC2 report, 2016), this depends mainly on the quality of the refurbishment plasterboard waste received, as current treatments have limited efficiency and customisation possibilities. As a result, the highest practical rate of incorporation of recycled gypsum in new plasterboards is currently around 20 wt%, since higher rates would also require higher use of costly additives (GtoG-DB4 report, 2016). Furthermore, there are water-soluble impurities present in gypsum, such as chloride, magnesium, sodium and potassium salts, that impact the bonding properties of gypsum crystals (Papailiopoulou et al., 2019). The GtoG project established that the concentration of these soluble salts in recycled gypsum must be less than 0.02 wt% (GtoG-DC2 report, 2016). But soluble salts that are encapsulated inside gypsum particles can appear at the gypsum surface due to particle attrition during processing. Therefore, the soluble salts content is affected by changes in gypsum particle size distribution during recycling and plasterboard manufacturing processes. Papailiopoulou et al. (2019) also pointed out that the uncertain soluble salt content of waste gypsum is one of the main market constraints for its utilisation in plasterboard manufacturing. However, there is no established criterion to determine recycled gypsum purity in terms of chemical composition. Therefore, it is necessary to define a criterion underpinned by previous research to determine the chemical purity of recycled gypsum. This will also enable the comparison of different gypsum purification processes to achieve high recycled gypsum purity, in terms of high dihydrate content and chemical purity, and optimisation of these processes to achieve shares of recycled gypsum in new plasterboards above 20 wt%. Two purification processes that could potentially be used to achieve this goal are hydrocyclone separation and acid leaching.

Hydrocyclones are simple equipment of easy operation and maintenance that are used to separate solids from a liquid medium. They are used in several industrial processes for the dewatering of slurries, including flue gas desulphurisation units to separate synthetic gypsum from other by-products. Hydrocyclones consist of a cylindrical section coupled to a conic section that has at its end an aperture called spigot. The suspension is introduced under pressure and tangentially to the cylindrical section,

which houses a coaxial tube called vortex finder. Most solid particles are carried in the underflow stream, which is discharged through the spigot. The remaining particles (fines) are carried in the overflow stream, which is discharged through the vortex finder (Svarovsky, 2000). The separation efficiency of the hydrocyclone is dictated by the particle size and density of the solid, solid concentration, mass flow rate, temperature of the liquid, presence of salts in the liquid, and diameters of hydrocyclone components. Hydrocyclone separation can be used to purify gypsum as soluble salts will dissolve in the liquid medium. In fact, hydrocyclones have been evaluated in the past to purify phosphogypsum (PG), which is obtained as a by-product in phosphoric acid plants. For instance, removal of soluble phosphorus, fluorine and organic matter was successful when using a PG/water ratio of 1:3 vol/vol and PG particle sizes less than 300  $\mu\text{m}$  (Singh et al., 1996).

Acid leaching is another purification process that has been evaluated to purify PG. This process is usually performed with sulphuric acid ( $\text{H}_2\text{SO}_4$ ), which is an unexpensive acid that yields more gypsum after neutralisation with  $\text{CaCO}_3$  (Tu et al., 2010; Jha et al., 2013). Usually, higher temperature and longer residence time during acid leaching increase the purification efficiency. Addition of salts, reduction of particle size and recirculation of the leaching solution, with and without acid addition between each cycle, might also increase the leaching efficiency. Kandil et al. (2017) found that the radium activity in PG was reduced 15% with an 8 M  $\text{H}_2\text{SO}_4$  solution when the slurry was stirred at 150 revolutions per minute for 30 minutes at 80 °C. In another work, rare earth metals in PG were leached with a dilute  $\text{H}_2\text{SO}_4$  solution and the purified gypsum was recrystallised into anhydrite with a concentrated  $\text{H}_2\text{SO}_4$  solution (Jarosinski et al., 1993). Other authors found that rare earth elements in PG were concentrated through double leaching with dilute  $\text{H}_2\text{SO}_4$  at 60 °C (Hammas-Nasri et al., 2016a; Hammam-Nasri et al., 2016b). However, Valkov et al. (2014) suggested that temperatures between 70 °C and 100 °C and residence times between 1 and 2 hours are required to extract rare earth metals in PG. During acid leaching, gypsum/liquid ratios lower than 1:3 wt/wt can make the process uneconomical due to the high amounts of process water, whereas gypsum/liquid ratios above 1 can cause operational issues due to the high viscosity of the gypsum slurry. Gypsum/liquid ratio of 1:3 wt/wt, using a 5 wt%  $\text{H}_2\text{SO}_4$  aqueous solution and stirring speed of 150 revolutions per minute with 3 L of slurry were found optimum for acid leaching of PG (Moalla et al., 2018).

As part of the ICEBERG project from the European Union's Horizon 2020 Research and Innovation Framework Programme under grant agreement No. 869336, the main aim of this work is to achieve high recycled gypsum purity (> 96 wt%) both in terms of dihydrate content and chemical purity with the development of a methodological approach based on hydrocyclone separation and acid leaching to minimise the detrimental effects of calcium sulphate hemihydrate and inorganic impurities on the properties of recycled gypsum from refurbishment plasterboard waste. Both purification processes have been evaluated individually and combined to achieve these purity targets. Simultaneously, a criterion to determine the chemical purity of gypsum is proposed.

## 2. MATERIALS AND METHODS

### 2.1 Materials

Refurbishment plasterboard waste was collected at a skip in Lenton Household Waste and Recycling Centre in Nottingham (United Kingdom) on the 15<sup>th</sup> of October 2020. The amount of plasterboard waste that was manually segregated and collected from the skip was approximately 30 kg. The plasterboard waste contained approximately 90 wt% gypsum and 10 wt% paper. Figure 1 shows that other materials were in contact with the refurbishment plasterboard waste in the skip (e.g. soil, plastics and wood), and that the plasterboard waste was exposed to the weather.

Sulphuric acid ( $\text{H}_2\text{SO}_4$ , Fisher Chemicals, certified analytical reagent, minimum purity 95 vol%) was used for acid leaching tests.

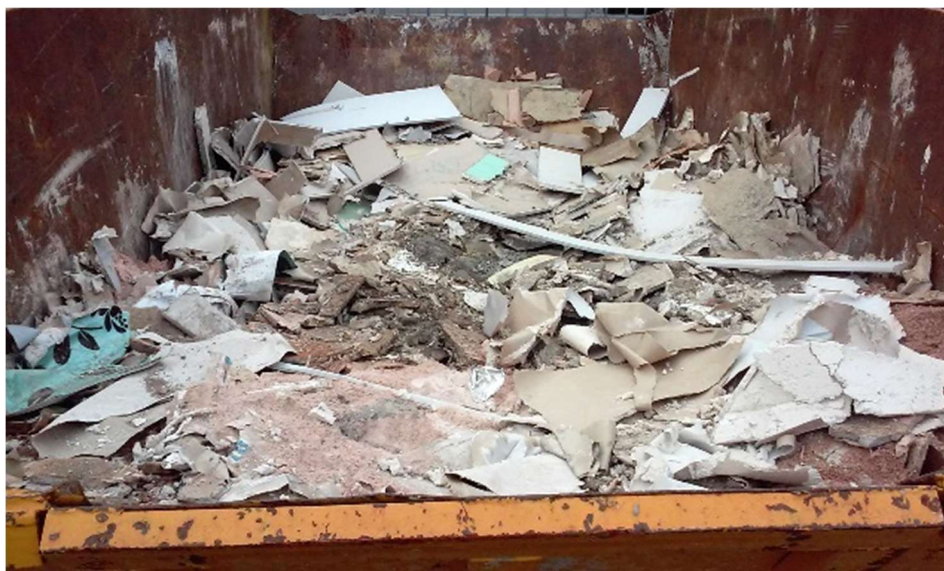


Figure 1. Skip with refurbishment plasterboard waste located at Lenton Household Waste and Recycling Centre (Nottingham, UK).

## 2.2 Laboratory work

### 2.2.1 Sample preparation

Gypsum particle sizes below  $250\ \mu\text{m}$  were prepared to: i) remove as many paper fibres as possible; and ii) increase the gypsum surface area to maximise the purification efficiency of hydrocyclone separation and acid leaching. Initially, the refurbishment plasterboard waste was crushed to particle sizes less than  $2000\ \mu\text{m}$ , with porcelain mortar and pestle, and sieved with a  $300\ \mu\text{m}$  sieve according to the standards ISO 3310-1 and BS 410-1. Then, the material passing was crushed again using the same method as before and sieved to obtain particle sizes less than  $250\ \mu\text{m}$ . This gypsum particle size fraction will be referred to as gypsum from refurbishment plasterboard waste (GRPW) hereafter. For the hydrocyclone separation test with GRPW,  $3.6\ \text{kg}$  of refurbishment plasterboard waste were crushed and sieved to obtain  $3.27\ \text{kg}$  of GRPW. For acid leaching tests, batches of  $750\ \text{g}$  of refurbishment plasterboard waste were crushed and sieved to produce enough amounts of GRPW to perform several tests (approximately  $100\ \text{g}$  per acid leaching test). It must be noted that GRPW contained less than  $0.5\ \text{wt}\%$  of paper fibres, which were mainly produced during the crushing stage. Some of the paper fibres generated during crushing agglomerated during the sieving stage, forming fluffy lumps that were easily removed. Furthermore, lining paper from the refurbishment plasterboard waste was segregated, broken down manually into small pieces, milled in a food blender to pulverise the paper fragments, and sieved to obtain  $21\ \text{g}$  of paper fines with particle sizes less than  $250\ \mu\text{m}$  to carry out a hydrocyclone test.

### 2.2.2 Hydrocyclone separation tests

A 2-inch Salter hydrocyclone, supplied with three vortex finder sizes and three spigot sizes, was used. All hydrocyclone components were made of polyurethane, which can withstand operating temperatures up to  $50\ ^\circ\text{C}$  but is not resistant to acid corrosion. Optimum operation of this hydrocyclone is achieved with  $15\ \text{wt}\%$  solids, with a maximum slurry capacity of  $3.8\ \text{m}^3/\text{h}$ . The hydrocyclone was assembled with a centrifugal pump and mixing tank, as shown in Figures 2a and 2b. Figure 2c shows the different hydrocyclone components and the inlet and outlet streams. All tests were performed with the recycle valve to the mixing tank fully open to maintain the gypsum particles dispersed in the tank. The hydrocyclone's inlet valve was fully open to operate at the highest possible capacity (around  $1.0\ \text{m}^3/\text{h}$ ). Preliminary tests with  $10\ \text{L}$  and  $30\ \text{L}$  of water in the mixing tank were performed to identify the configurations of vortex finder and spigot sizes that provided optimum flow patterns at the hydrocyclone's



underflow (i.e., between roping and spraying discharge). Vortex finder sizes of 9, 11 and 14 mm and spigot sizes of 3.2, 4.5 and 9.4 mm were used, and the nine possible combinations were evaluated. Only combining vortex finder sizes of 11 and 14 mm and spigot sizes of 4.5 and 9.4 mm provided optimum water flow patterns. The volumetric water flow rate in the underflow and the underflow/overflow volumetric flow ratio when using these four configurations was also determined. The highest flow rates and underflow/overflow ratios were obtained with the 9.4 mm spigot. The configuration of vortex finder size of 14 mm and spigot size of 9.4 mm was chosen for the tests with paper fibres and GRPW because the underflow/overflow volumetric flow ratio was closer to 1. The paper fibre slurry was prepared by filling the mixing tank with 20 L of municipal water and adding the 21 g of paper fibres with particles sizes less than 250  $\mu\text{m}$ . The test with paper fibres was performed to elucidate whether this impurity, which has a density below 1,600  $\text{kg/m}^3$  (Montero et al., 2010), can be separated from gypsum, which has a density of 2,300  $\text{kg/m}^3$ , when passing through the hydrocyclone. The GRPW slurry was prepared by filling the mixing tank with 18.6 L of municipal water and adding 3.27 kg of GRPW. The test with GRPW lasted 3 hours and samples were collected at the underflow every hour and for a period of 5 seconds to quantify the volumetric and mass flow rates. A sample was also collected at the overflow after 3 hours of operation.

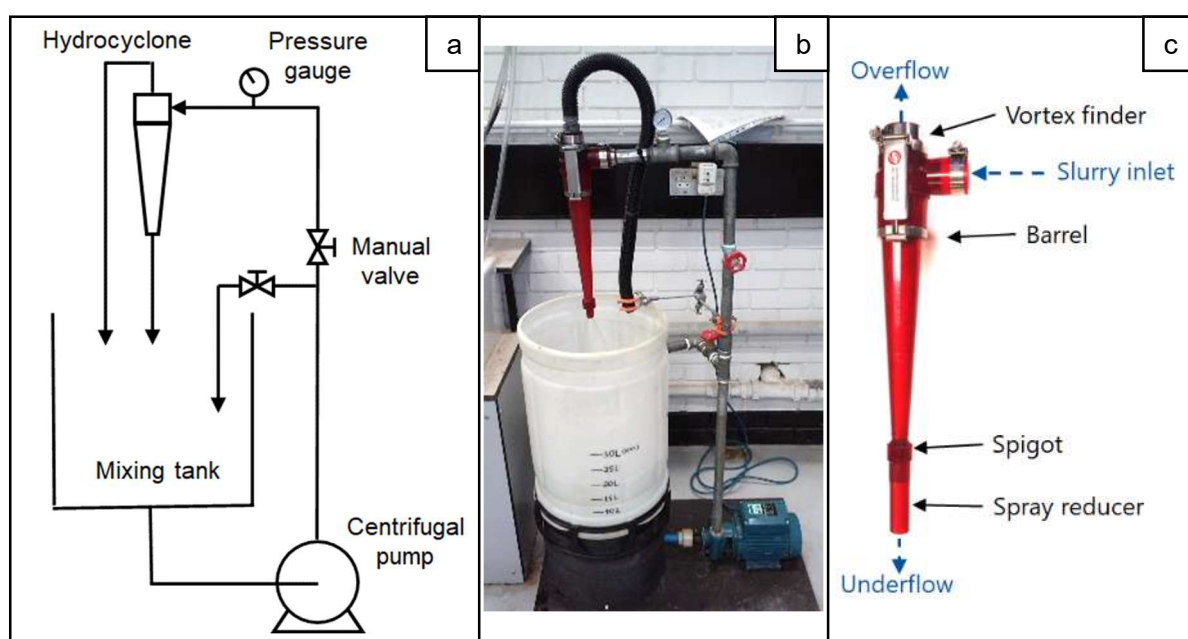


Figure 2. Schematic representation of hydrocyclone separation setup (a), actual lab-scale hydrocyclone separation setup (b) and 2-inch Salter hydrocyclone components and streams (c).

### 2.2.3 Acid leaching tests

Acid leaching tests were performed with a borosilicate beaker, a hot plate and an overhead stirrer placed inside a fume cupboard. Distilled or purified water was used to prepare the acidic solutions. The temperature of the slurry was measured with an independent thermocouple placed inside the beaker. Acid leaching tests were conducted with a GRPW/solution ratio of 1:3 wt/wt, with a slurry volume of 350 mL and a stirring speed of 150 revolutions per minute. Acid leaching was performed at temperatures of 24 °C, 60 °C and 90 °C, residence times of 30 minutes, 1 hour, 1.5 hours, 2 hours and 3 hours, and with sulphuric acid concentrations of 3 wt% (0.3 M), 5 wt% (0.5 M) and 10 wt% (1.1 M) in aqueous solutions. The GRPW sample was added to the acidic solution at room temperature and the slurry was heated to the target temperature at a rate of 3-4 °C/min. The impact of higher stirring speed (300 revolutions per minute), slurry volume (2000 mL) and heating rate (addition of GRPW to solution already at target temperature) on the chemical purity of the treated material was also evaluated. At the end of each acid leaching test, the slurry was cooled down to room temperature prior filtration. Furthermore, the GRPW sample collected at the hydrocyclone's underflow after a residence time of 3 hours was also used as

feedstock for an acid leaching test to ascertain the effect of combining hydrocyclone separation with acid leaching.

#### *2.2.4 Filtration and drying*

Treated GRPW samples from hydrocyclone separation and acid leaching tests were filtrated using a Buchner filtration kit connected to a vacuum pump. Only in the case of acid leaching tests, distilled or purified water was used to wash the gypsum cake until the pH of the filtrate was around 6. Samples were dried in an oven at 45 °C for either 12 or 24 hours, depending on the water content of the cakes. The temperature was kept at 45 °C to prevent conversion of calcium sulphate dihydrate to calcium sulphate hemihydrate. Finally, the dried samples were crushed with ceramic mortar and pestle to produce a powder for further characterisation.

### **2.3 Sample characterisation**

#### *2.3.1 X-ray fluorescence*

The chemical composition of the samples was determined through X-ray fluorescence (XRF). XRF analysis was performed with a Orbis micro-XRF spectrometer. Sample pellets were prepared by blending 0.8 g of gypsum powder with 0.2 g of boric acid (binder) powder. This blend was placed in a die and piston of 5 mm in diameter and compacted in a manual hydraulic press applying 10 tonnes of force to produce the pellet. XRF data were acquired under vacuum in five regions of the pellet using a voltage of 30 kV, current of 0.4 mA, amplifier time of 1.6  $\mu$ s and acquisition time of 120 seconds. The weight percentages of SO<sub>3</sub>, CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MnO, MgO, P<sub>2</sub>O<sub>5</sub>, K<sub>2</sub>O, Na<sub>2</sub>O, Ni<sub>2</sub>O<sub>3</sub>, SrO and Cl were recorded. MgO, P<sub>2</sub>O<sub>5</sub>, K<sub>2</sub>O, Na<sub>2</sub>O and Cl have been identified as detrimental for plasterboard manufacturing (Rashad, 2017; Papailiopoulou et al., 2019). A natural gypsum currently used in plasterboard manufacturing was used as reference to define the criterion for the calculation of waste gypsum purity through X-ray fluorescence. This natural gypsum has 56.6 wt% SO<sub>3</sub>, 33.3 wt% CaO, 3.7 wt% SiO<sub>2</sub>, 1.1 wt% Al<sub>2</sub>O<sub>3</sub>, 0.4 wt% Fe<sub>2</sub>O<sub>3</sub>, 0.1 wt% MnO, 1.6 wt% MgO, 1.5 wt% P<sub>2</sub>O<sub>5</sub>, 0.3 wt% K<sub>2</sub>O, 0.7 wt% Na<sub>2</sub>O, 0.6 wt% Cl and traces of Ni<sub>2</sub>O<sub>3</sub> and SrO. The MnO content in GRPW (0.3 wt%) was higher than that in the natural gypsum (0.1 wt%). On the contrary, the amounts of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Ni<sub>2</sub>O<sub>3</sub> and SrO in GRPW were lower than or similar to the amounts in the natural gypsum. Therefore, gypsum purity was calculated as the sum of SO<sub>3</sub>, CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Ni<sub>2</sub>O<sub>3</sub> and SrO contents in the samples. The mean standard deviation of the purity values was also calculated. Furthermore, the content of CaSO<sub>4</sub> (CaO+SO<sub>3</sub>) was determined to differentiate between samples with similar chemical purity values.

#### *2.3.2 Thermal gravimetric analysis and derivative thermogravimetry*

The calcination behaviour of the samples was determined through thermal gravimetric analysis (TGA) and derivative thermogravimetry (DTG). TGA/DTG were performed with a TA Q5000IR thermo-analyzer (TA Instruments Inc., US). An amount of 20 mg was placed in a sealed aluminium pan with a pierced lid and heated from 40 °C to 250 °C using a heating rate of 5 °C/min. A nitrogen flow rate of 20 mL/min was applied on the balance throughout the test. Since pure CaSO<sub>4</sub>·2H<sub>2</sub>O loses 20.93 wt% upon heating to 240 °C, the theoretical calcium sulphate dihydrate content was calculated using TGA data by multiplying the sample weight loss at 240 °C by a factor of 4.778.

## **3. RESULTS AND DISCUSSION**

The hydrocyclone separation test with 21 g of paper fibres, 20 L of municipal water, using the 14 mm vortex finder and 9.4 mm spigot, showed that 57 wt% of the fibres entering the hydrocyclone were directed to the underflow. The hydrocyclone separation test with GRPW was performed with the same

hydrocyclone configuration, using 20 L of slurry composed of 18.6 L of municipal water and 3.27 kg of GRPW (15 wt% GRPW). This slurry produced a foam throughout the test, as shown in Figure 3. The temperature of the slurry increased slightly from 21 °C at the beginning of the test to 24 °C after 3 hours, which was caused by heat transfer from the centrifugal pump. Results showed that 58 wt% of GRPW entering the hydrocyclone was directed to the underflow, which is almost identical to the amount of paper fibres directed to the underflow when using this impurity alone. Therefore, the 2-inch hydrocyclone used in this study could not separate the paper fibres in GRPW.



Figure 3. Operation of hydrocyclone separation setup with slurry containing 15 wt% GRPW (left) and foam produced during the test (right).

GRPW samples were collected at the underflow after 1, 2 and 3 hours. A sample was also collected at the overflow after 3 hours. The four GRPW samples were filtrated, dried, and characterised through XRF to determine the purity and  $\text{CaSO}_4$  content of the samples. Figure 4 shows that the two-step crushing and sieving methodology is a very effective strategy to achieve around 96 wt% chemical purity in the GRPW feedstock.

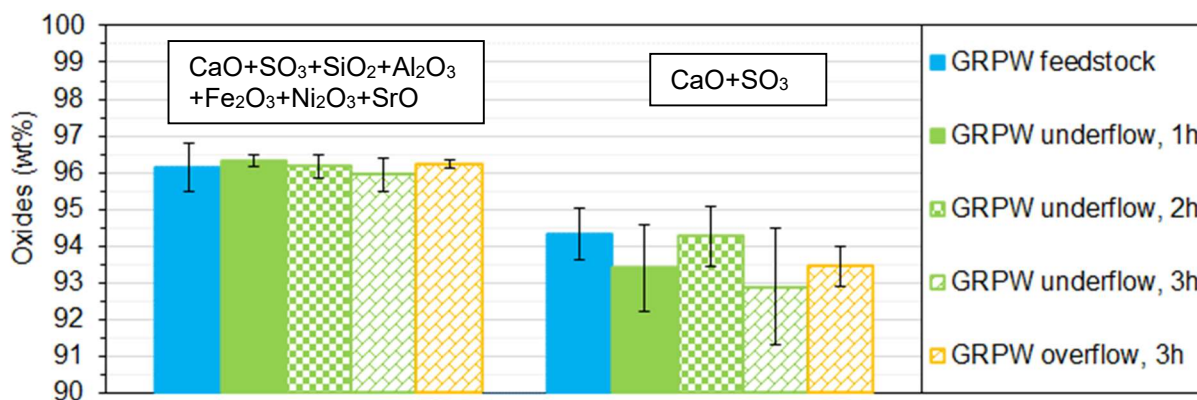


Figure 4. Purity (left) and  $\text{CaSO}_4$  content (right) of GRPW feedstock and samples collected at the hydrocyclone's underflow and overflow at different residence times.

However, the results also indicate that the purity of the samples collected at the hydrocyclone's underflow is around 96 wt% within experimental error, suggesting that hydrocyclone separation is not effective for GRPW purification. The standard deviation values obtained with CaO and  $\text{SO}_3$  were much higher than those obtained when calculating the purity values, i.e., with the inclusion of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Ni}_2\text{O}_3$  and SrO. It was observed that this is mainly due to fluctuations in  $\text{SiO}_2$  content at different positions of the sample pellet analysed through XRF.

The results from acid leaching tests using different temperatures, residence times and  $\text{H}_2\text{SO}_4$  solutions are presented in Figure 5. There are no significant differences in the purity values of the acid-leached



samples (around 96.5 wt%) but, in general, these values are 0.5-1 wt% higher than that of the GRPW feedstock. These results might suggest that acid leaching at 60 °C for 30 minutes using a 3 wt%  $H_2SO_4$  solution would be suitable to achieve recycled GRPW with more than 96 wt% purity.

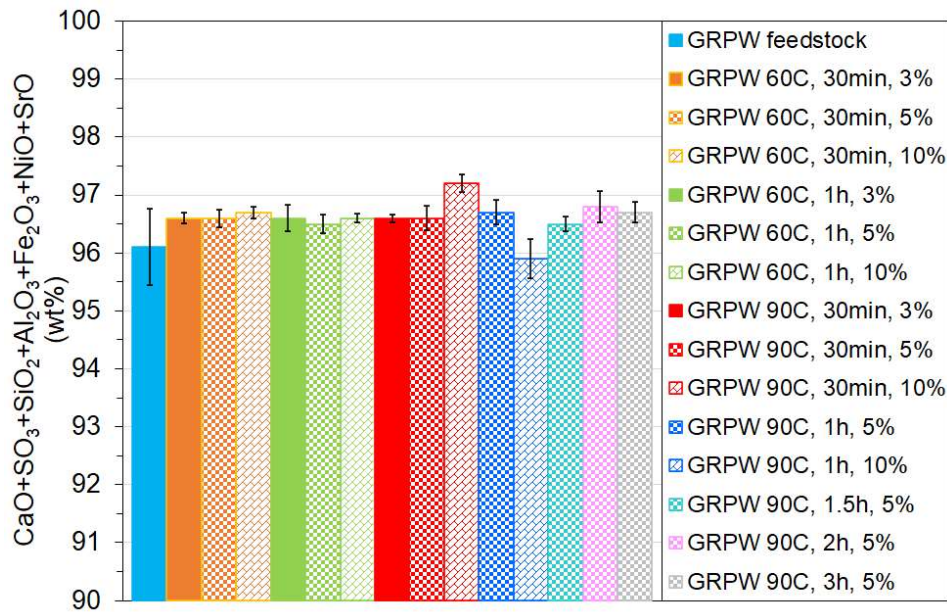


Figure 5. Purity of the GRPW feedstock before and after acid leaching using different temperatures, residence times and  $H_2SO_4$  solutions.

However, Figure 6 shows that the  $CaSO_4$  content of samples leached at 60 °C is usually lower than the  $CaSO_4$  content of samples leached at 90 °C. The lower  $CaSO_4$  content observed in some samples after acid leaching at 60 °C and 90 °C compared to the that of the GRPW feedstock could be explained by the Ostwald ripening process. This process consists of the initial dissolution of small gypsum crystals followed by the redeposition of dissolved calcium sulphate on the surfaces of larger crystals. This phenomenon was observed by Zheng et al. (2020) during acid leaching under hydrothermal conditions at 100-120 °C of a chromium-containing gypsum waste.

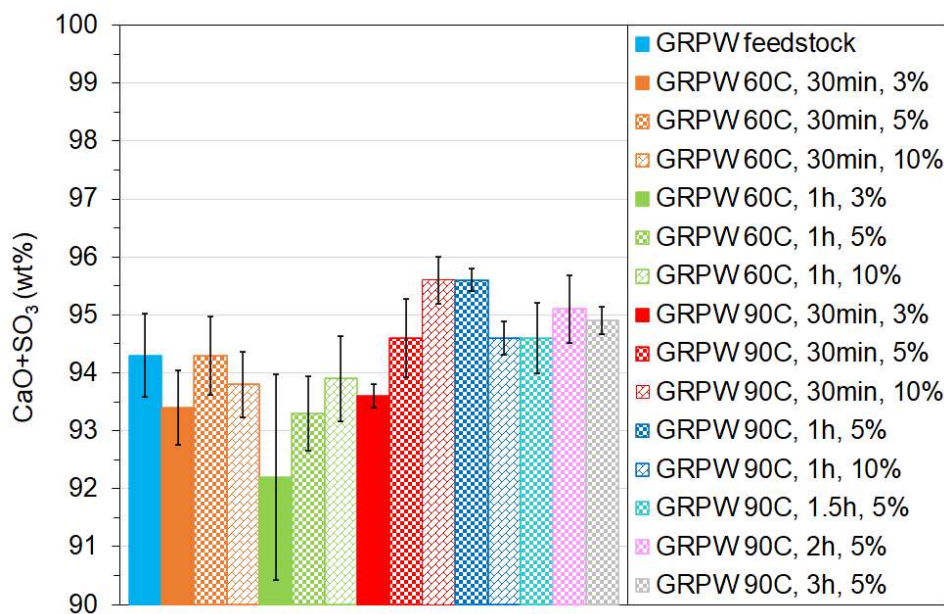


Figure 6.  $CaSO_4$  content of the GRPW feedstock before and after acid leaching using different temperatures, residence times and  $H_2SO_4$  solutions.

The  $\text{CaSO}_4$  content reaches a maximum of 95.5 wt% when acid leaching is carried out at 90 °C, either for 30 minutes using a 10 wt%  $\text{H}_2\text{SO}_4$  solution or for 1 hour using a 5 wt%  $\text{H}_2\text{SO}_4$  solution. It could be argued that best conditions for acid leaching are the latter. Under these acid leaching conditions (90 °C, 1 hour and 5 wt%  $\text{H}_2\text{SO}_4$ ),  $\text{P}_2\text{O}_5$  and  $\text{MnO}$  contents in GRPW did not change, but  $\text{Na}_2\text{O}$  content and  $\text{K}_2\text{O}$  content decreased by 76%, and  $\text{MgO}$  content and  $\text{Cl}$  content decreased by 37%.

An acid leaching test was also performed on the GRPW sample collected at the hydrocyclone's underflow after 3 hours. This test was carried out to elucidate whether the hydrocyclone separation process can further improve the acid leaching efficiency at 90 °C for 1 hour using a 5 wt%  $\text{H}_2\text{SO}_4$  solution. Figure 7 indicates that the purity of the sample collected at the hydrocyclone's underflow increases to 97 wt% after acid leaching, being this purity slightly higher than that with the acid leaching test alone (96.7 wt%, Figure 5). However, the  $\text{CaSO}_4$  content (94.4 wt%) is similar to that in the GRPW feedstock and 1 wt% lower than that in GRPW after acid leaching alone (95.6 wt%, Figure 6). These results indicate that the implementation of a hydrocyclone separation plant prior the acid leaching process is impractical.

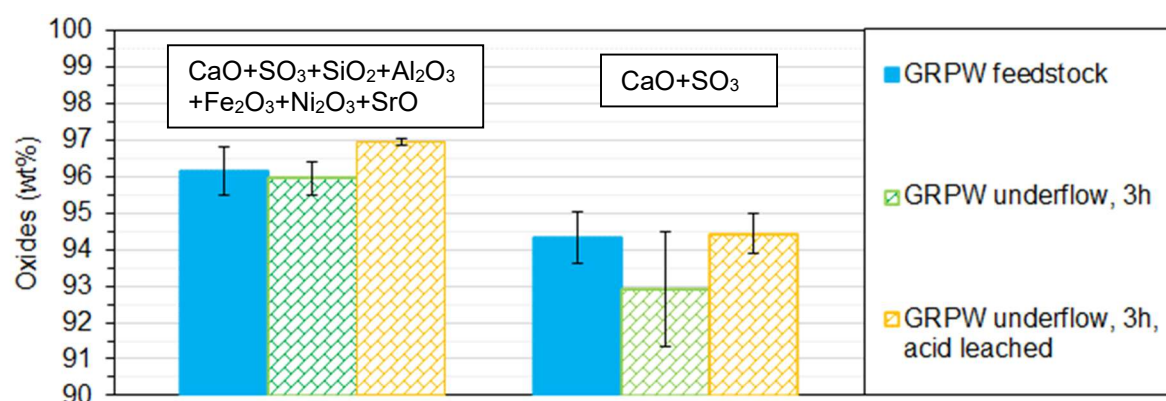


Figure 7. Purity (left) and  $\text{CaSO}_4$  content (right) of the GRPW feedstock and the sample collected at the hydrocyclone's underflow after 3 hours before and after acid leaching at 90 °C for 1 hour using a 5 wt%  $\text{H}_2\text{SO}_4$  solution.

An increase in stirring speed from 150 to 300 revolutions per minute did not have any impact on the purity of the treated GRPW. However, pre-heating the 5 wt%  $\text{H}_2\text{SO}_4$  solution to 90 °C before adding the GRPW feedstock did not change the chemical composition of the material. This finding suggests that the impurities are dissolved during the heating period (i.e., around 15 minutes from room temperature to 90 °C). Finally, a test was performed with 2000 mL of slurry, with a stirring speed of 250 revolutions per minute to maintain GRPW in suspension. The other acid leaching parameters were kept constant (90 °C, 1 hour, 5 wt%  $\text{H}_2\text{SO}_4$  solution, GRPW/solution ratio of 1:3 wt/wt). It was found that the purity of the treated sample using 2000 mL of slurry was similar to that of the treated sample using 350 mL of slurry.

Acid leaching at 90 °C for 1 hour using a 5 wt%  $\text{H}_2\text{SO}_4$  solution has led in this work to more than 96 wt% purity in the recycled GRPW. According to another quality target, the calcium sulphate dihydrate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) content in the recycled GRPW should be higher than 96 wt%. In this study, the  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  content was calculated theoretically using TGA data. Figure 8 displays the TGA and DTG profiles for the GRPW feedstock before and after acid leaching at 90 °C for 1 hour using a 5 wt%  $\text{H}_2\text{SO}_4$  solution. Acid leaching causes an increase in weight loss of around 0.5 wt% at 240 °C, which could be caused by the removal of impurities and the increase in  $\text{CaSO}_4$  content seen in Figures 5 and 6, respectively. The first devolatilisation peak at around 135 °C in the DTG profiles (peak 1) is associated to the removal of water when  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  converts into  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ . The second devolatilisation peak (peak 2) corresponds to the removal of water when  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  converts into  $\text{CaSO}_4$ . The DTG profiles of both samples are similar, showing only a small reduction in the maximum devolatilisation rates (peaks 1 and 2) after acid leaching. The  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  contents in GRPW feedstock and GRPW after acid leaching determined with TGA data were 93.0 wt% and 96.3 wt%, respectively. Therefore, acid leaching of GRPW at 90 °C for 1 hour using a 5 wt%  $\text{H}_2\text{SO}_4$  solution increases the  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  content above 96

wt%. Future work will focus on the mechanical properties of the recycled gypsum to validate its application in plasterboard manufacturing.

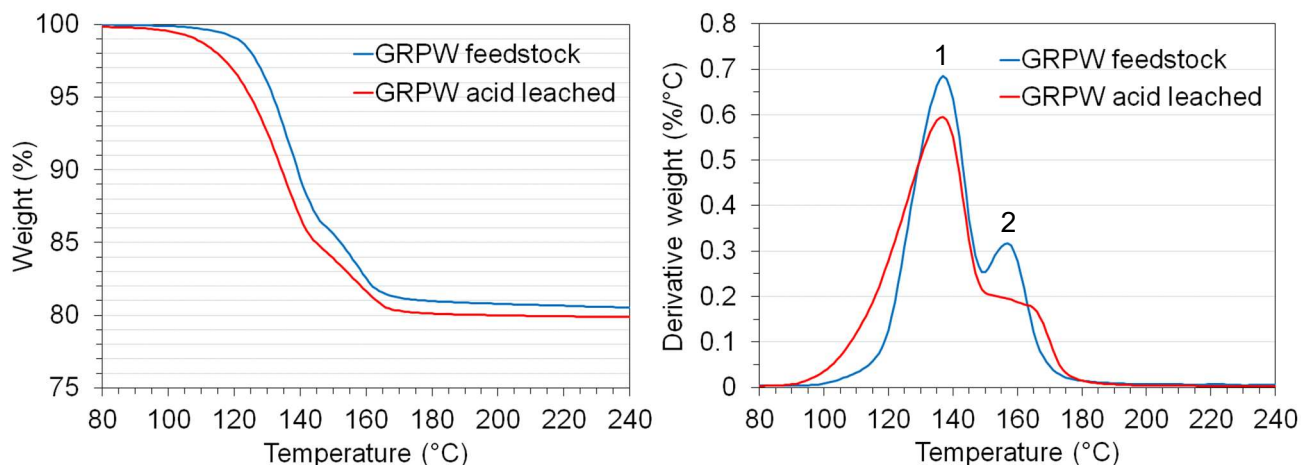


Figure 8. TGA and DTG profiles of the GRPW feedstock before and after acid leaching at 90 °C for 1 hour using a 5 wt% H<sub>2</sub>SO<sub>4</sub> solution.

#### 4. CONCLUSIONS

Hydrocyclone separation and acid leaching have been evaluated separately and combined to achieve calcium sulphate dihydrate (CaSO<sub>4</sub>·2H<sub>2</sub>O) content and chemical purity in recycled gypsum from refurbishment plasterboard waste above 96 wt%. The chemical purity of gypsum was calculated in this work as the sum of SO<sub>3</sub>, CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Ni<sub>2</sub>O<sub>3</sub> and SrO contents. The main findings of this work are:

- Hydrocyclone separation at room temperature for up to 3 hours did not have any significant impact on the chemical composition of gypsum from refurbishment plasterboard waste. Therefore, this process alone is not effective for waste gypsum purification.
- Acid leaching of gypsum from refurbishment plasterboard waste at 90 °C, for either 30 minutes using a 10 wt% H<sub>2</sub>SO<sub>4</sub> solution or 1 hour using a 5 wt% H<sub>2</sub>SO<sub>4</sub> solution, achieved 96.5 wt% chemical purity and 95.5 wt% CaSO<sub>4</sub> in the recycled material.
- An increase in stirring speed or slurry volume did not impact the efficiency of the acid leaching process. On the contrary, adding the waste gypsum to the acidic solution at 90 °C prevented the removal of impurities. Therefore, the impurities in gypsum from refurbishment plasterboard waste were dissolved during the heating stage of the acid leaching process.
- The recycled gypsum obtained after acid leaching at 90 °C for 1 hour using a 5 wt% H<sub>2</sub>SO<sub>4</sub> solution also had a calcium sulphate dihydrate content above 96 wt%.
- Acid leaching of the sample from the hydrocyclone's underflow after 3 hours residence time had slightly higher purity (97 wt%) than that of the waste gypsum feedstock after acid leaching (96.7 wt%). However, its CaSO<sub>4</sub> content (94.4 wt%) was similar to that of the waste gypsum feedstock and much lower than that in the acid-leached gypsum (95.6 wt%). Therefore, there is no technical advantage in the use of hydrocyclone separation for the purification of gypsum from refurbishment plasterboard waste.
- Overall, crushing and sieving of refurbishment plasterboard waste to less than 250 μm, followed by the preparation of a slurry with gypsum/solution ratio 1:3 wt/wt, and acid leaching in a stirred and

heated tank (heating rate of 3–4 °C/min) at 90 °C for 1 hour using a 5 wt% H<sub>2</sub>SO<sub>4</sub> solution will produce recycled gypsum from refurbishment plasterboard waste with calcium sulphate dihydrate content and chemical purity values above 96 wt%.

## ACKNOWLEDGEMENTS

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869336. The authors would also like to acknowledge the use of XRF and TGA facilities within the Loughborough Materials Characterisation Centre at Loughborough University.

## REFERENCES

- BSI PAS 109, 2013. Specification for the production of reprocessed gypsum from waste plasterboard. BSI Standards Limited.
- GtoG-DB4 report (2016). Production process parameters. LIFE 11 ENV/BE/001039. <https://gypsumtogypsum.org/download-the-gtog-reports-now/>
- GtoG-DC2 report (2016). Protocol of action B2.2: Quality criteria for recycled gypsum, technical and toxicological parameters. LIFE11 ENV/BE/001039. <https://gypsumtogypsum.org/download-the-gtog-reports-now/>
- Hammas-Nasri, I., Horchani-Naifer, K., Férid, M., 2016a. Rare earths concentration from phosphogypsum waste by two-step leaching method. *Int. J. Miner. Process.* 149, 78–83. <https://doi.org/10.1016/j.minpro.2016.02.011>
- Hammas-Nasri, I., Horchani-Naifer, K., Férid, M., Barca, D., 2016b. Rare earths concentration from phosphogypsum waste by two-step leaching method. *Int. J. Miner. Process.* 149, 78–83. <https://doi.org/10.1016/j.minpro.2016.02.011>
- Jarosinski, A., Kowalczyk, J., Mazanek, C., 1993. Development of the Polish wasteless technology of apatite phosphogypsum utilization with recovery of rare-earths. *J. Alloy. Compd.* 200, 147–150. [https://doi.org/10.1016/0925-8388\(93\)90485-6](https://doi.org/10.1016/0925-8388(93)90485-6)
- Jha, M.K., Lee, J.-C., Kim, M.-S., Jeong, J., Kim, B.-S., Kumar, V., 2013. Hydrometallurgical recovery/recycling of platinum by the leaching of spent catalysts: A review. *Hydrometallurgy* 133, 23–32. <https://doi.org/10.1016/j.hydromet.2012.11.012>
- Jiménez-Rivero, A., García-Navarro, J., 2016. Indicators to measure the management performance of end-of-life gypsum: from deconstruction to production of recycled gypsum. *Waste Biomass Valori.* 7, 913–927. <https://doi.org/10.1007/s12649-016-9561-x>
- Jiménez-Rivero, A., García-Navarro, J., 2017. Characterization of quality recycled gypsum and plasterboard with maximized recycled content. *Mater. Construcc.* 67, e137. <https://doi.org/10.3989/mc.2017.06016>
- Kandil, A.-H.T., Cheira, M.F., Gado, H.S., Soliman, M.H., Akl, H.M., 2017. Ammonium sulfate preparation from phosphogypsum waste. *J. Radiat. Res. Appl. Sci.* 10, 24–33. <https://doi.org/10.1016/j.jrras.2016.11.001>
- Kuntze, R.A., 2009. Gypsum. Connecting Science and Technology. ASTM International, Newburyport, Massachusetts, USA.
- Lushnikova, N., Dvorkin, L., 2016. Sustainability of gypsum products as a construction material. In: *Sustainability of Construction Materials*. 2nd edition Ed. Jamal Khatib. Woodhead Publishing, Cambridge, UK, pp. 643–681.
- Moalla, R., Gargouri, M., Khmiri, F., Kamoun, L., Zairi, M. 2018. Phosphogypsum purification for plaster production: A process optimization using full factorial design. *Environ. Eng. Res.* 23, 36–45. <https://doi.org/10.4491/eer.2017.055>
- Montero, A., Tojo, Y., Matsuo, T., Matsuto, T., Yamada, M., Asakura, H., Ono, Y., 2010. Gypsum and organic matter distribution in a mixed construction and demolition waste sorting process and their possible removal from outputs. *J. Hazard. Mater.* 175, 747–753. <https://doi.org/10.1016/j.jhazmat.2009.10.072>
- Papailiopoulou, N., Grigoropoulou, H., Founti, M., 2019. Techno-economic impact assessment of recycled gypsum usage in plasterboard manufacturing. *J. Remanuf.* 9, 141–167. <https://doi.org/10.1007/s13243-018-0062-x>

- Rashad, A.M., 2017. Phosphogypsum as a construction material. *J. Clean. Prod.* 166, 732–743.  
<http://dx.doi.org/10.1016/j.jclepro.2017.08.049>
- Singh, M., Garg, M., Verma, C.L., Handa, S.K., Kumar, R., 1996. An improved process for the purification of phosphogypsum. *Constr. Build. Mater.* 10, 597–600. [https://doi.org/10.1016/S0950-0618\(96\)00019-0](https://doi.org/10.1016/S0950-0618(96)00019-0)
- Svarovsky, L., 2000. Solid-liquid separation. 4th edition, Elsevier.
- Tu, Y.-J., Chang, C.-K., You, C.-F., Lou, J.-C., 2010. Recycling of Cu powder from industrial sludge by combined acid leaching, chemical exchange and ferrite process. *J. Hazard. Mater.* 181, 981–985.  
<https://doi.org/10.1016/j.jhazmat.2010.05.111>
- Valkov, A.V., Andreev, V.A., Anufrieva, A.V., Makaseev, Y.N., Bezrukova, S.A., Demyanenko, N.V., 2014. Phosphogypsum technology with the extraction of valuable components. *Procedia Chem.* 11, 176–181.  
<https://doi.org/10.1016/j.proche.2014.11.031>