PROSPECTS OF RECYCLING USED PLASTER OF PARIS – SHORT REVIEW

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Abstract

Plaster of Paris (POP- CaSO4. 0.5H2O) is used for various applications, such as in the ceramic industry, where it serves as a crucial component in crafting moulds and cementitious materials used in construction projects such as wall plaster, wall boards, and gypsum blocks. The dental industry uses POP for mounting casts or models of oral tissues. POP is commonly used in orthopaedic applications to support fractures for broken bones, making positive casts/models for fabricating mobility assistive devices. Demand for POP is continuously increasing with the expansion of the mentioned industries. Notwithstanding this sizable market, POP disposal has become a serious concern. Conventional POP disposal techniques, such as burning and dumping in landfills, negatively impact the environment by causing groundwater contamination, air pollution, disturbance of habitats, and land use issues. In this regard, this review focuses on the possible recyclability of POP. POP recycling is typically done by calcining used POP at relatively higher temperatures (150-1800C), where dehydration of used POP (CaSO4.2H2O) becomes recycled POP (CaSO4.0.5H2O). Many other factors, such as temperature and curing time, particle size, sample size, POP-to-water ratio, method of recycling, and secondary additives, affect the quality of recycled POP. Recycling reduces the need for virgin materials, conserves natural resources, and minimizes the environmental impact of extraction and production, encouraging the circular economy.

Keywords: Plast of Paris, Gypsum, Waste Management, Recycling, Circular economy

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Introduction

According to the literature, Plaster of Paris (POP), the name originated as it was mined on a large scale from Montmartre in the Paris district. Nevertheless, as POP was inside the pyramids, it has been assumed that they had been used even before the Industrial Revolution. POP took place in society when their previous materials, such as wooden sticks, bamboo, wax, starch, and cardboard, failed in their tasks (Sharma & Prabu, 2013).

1.1 Production of POP

POP ($CaSO_4$. $0.5H_2O$) has been derived by calcining gypsum ($CaSO_4$. $2H_2O$). Gypsum deposits are mainly found in the United States of America, France, West Germany, Poland, and Austria (Lokuliyana et al., 1988). There are two types of gypsum in the world: 1 natural and 2. synthetic.

1.1.1 Natural Gypsum

Natural gypsum mainly consists of calcium sulphate which is known as a non-metallic mineral deposit as fairly soft and impure rock. These depositions mostly depend on pressure, temperature, and concentrations of salts, which can be recovered using quarries and shallow underground mines. Natural gypsum comes with the colour of white or light grey. It can be pink, dark grey, or almost black depending on the impurities present (Matani, 2017).

1.1.2 Synthetic Gypsum

It is also identical to natural chemical and crystal structural gypsum. The difference is in the physical state, which lies in the origin or the formation method. Usually, synthetic gypsum is obtained as the final stage of industrial processes, which is finely divided but contains more free water than natural gypsum. The water must be removed by drying (Matani, 2017).

The chemical transformation of gypsum during the calcination process is shown in Equation (1). With the control of thermal treatment, $CaSO_4$. $2H_2O$ loses ~75% of the water included and produces POP ($CaSO_4.0.5H_2O$). Once the hemihydrate contacts with water, the reaction works reverse and transforms into the di-hydrated form, as shown in Equation (2). (Geraldo et al., 2017).

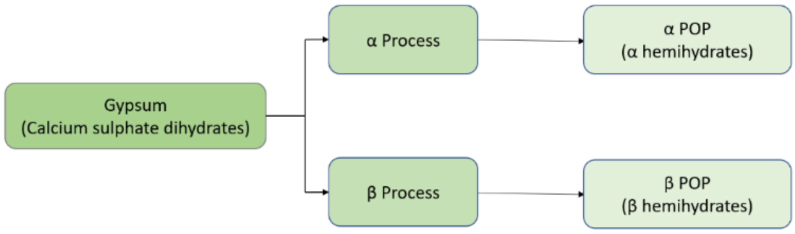
$$CaSO_4.\ 2H_2O \xrightarrow{125^0C\text{-}180^0C} CaSO_4.\ 0.5H_2O + 1.5H_2O \qquad \text{Eq. (1)}$$

$$CaSO_4.\ 0.5H_2O + 1.5H_2O \longrightarrow CaSO_4.\ 2H_2O + \text{Heat} \qquad \text{Eq. (2)}$$

POP is typically produced by calcining gypsum at temperatures ranging from 120 ^{0}C to 180 ^{0}C. However temperature up to 400 ^{0}C is also reported in the literature (Geraldo et al., 2017; Matani, 2017). It was stated that the structure, properties, and final quality depend on the calcination conditions such as temperature, pressure, and rapidity. According to the dehydration conditions of gypsum, two types of POPs are produced by two calcination processes (Figure 1).

Figure 1.

Hemihydrates Formation Process



1.1.3 α Process and α-POP

α-POP is formed under normal atmospheric conditions, independent of water vapor pressure. It has a high mechanical strength compact crystal types with low water demand. Due to the high mechanical strength, alpha-type POP is mostly used in industrial plaster formulations. It has a compact crystal structure with a low specific surface can produce hard and low porosity casts with low water demand (Kuntze, 2009).

1.1.4 β Process and β -POP

β-POP is obtained either by autoclaving or by solution processes. Water demands and specific surface area are higher in β-POP crystals and are also porous but with low mechanical properties. They are ideal for lightweight buildings or moulds in ceramic applications due to their absorbent properties(Kuntze, 2009). Studies show that β hemihydrate could consist of $CaSO_4.0.5H_2O$, anhydrite III – unstable, anhydrite II – insoluble, calcium sulphate dihydrate ($CaSO_4$.$2H_2O$), and a small amount of impurities (Pinheiro & Camarini, 2015).

It was reported that during the dehydration of gypsum for commercial POP, β-hemihydrate formed in temperatures ranging between 100 °C and 180 °C. Anhydrite III forms in temperatures below 300^0C. POP used in construction has both compounds hemihydrate and anhydrite III (Bardella & Camarini, 2012)

1.2 Market Size of POP

Global Gypsum Market was valued at USD 7.85 billion in 2023, which is the raw material of the POP, and is projected to register a compound annual growth rate (CAGR) of 6.2% by 2033, reaching USD 13.76. Accelerating the growth of the construction industry, increasing urban migration, and rising consumer spending on advanced construction materials are the factors augmenting the market growth (Katiwade, 2021). Despite the promising growth in the industry, the management of waste POP has become a challenge, causing many environmental and social issues.

1. **Waste Management of POP**

After the use, most POP are openly dumped or sent to landfills. In landfills, wet gypsum within POP undergoes dissolution, transforming into calcium and sulphate, potentially seeping into groundwater and resulting in sulphate contamination. The U.S. federal drinking water standard stimulates a sulphate limit of 250 mg/L, a threshold that has occasionally been exceeded in groundwater near untreated landfills. Moreover, the disposal of POP can contribute to elevated concentrations of Total Dissolved Solids (TDS) in numerous construction and demolition debris landfill sites. The current environmental delusions processed by large multinational companies who process POP have disregarded the importance of recycling or reusing materials for their own benefits as well as the corporate social responsibilities. Improper disposal of plaster in Paris has a major impact on the environment. This mini-review research article focuses on the prospects of recycling used POP from ceramic models. Mainly, focus on the possibilities to recycle POP and the factors affecting the Process. The number of recent research publications relevant to POP recycling was evaluated systematically for the review article.

2.1 Recycling and Reusing of POP Models

Most POP-used waste in industries like ceramic, medical and construction are being recycled in various ways. In building construction, POP is used for different applications such as renders, plates, pieces for decoration, dry walls, and blocks. Plasters for commercial applications are used for excellent performance, a pleasing appearance, easy application, and promoting a healthy environment for occupants. Plasters are used in the construction industry in a way that results in significant material wastage. Based on the initial amount of plaster used, the medium values of this waste production range from 18 to 35 % and can reach values higher than 45 % (Camarini et al., 2011).

Recycling of the commercial plaster waste was typically done by calcining at temperatures of 150 to 200 °C for at least 24 h. This process dehydrates the POP, and recycled POP is produced (Camarini et al., 2011).

In another study, commercial POP waste was collected and calcined at the temperature of 150°C ± 5°C for one hour. The results from the study clearly indicated that the mechanical properties of the recycled POP are better than the original POP, and the increased number of recycling cycles resulted in reduced setting time (time taken to harden the POP) (Geraldo et al., 2017).

In the ceramic industry, moulds are created by mixing POP with water in pre-defined ratios (i.e., Equation 02). POP moulds can absorb water, and the produced moulds have higher strength. The quality of the POP moulds affects the quality of the final ceramic product. POP moulds must have a capillary effect to absorb water and proper strength and accurate dimension with a cavity-free smooth surface. The possibility of adding POP waste as a filler substituting silica was studied for the ceramic industry. The results revealed that adding 2-10% (wt) of POP waste could increase the percentage of shrinkage and porosity of ceramic (Badarulzaman et al., 2015)

It was highlighted in medical waste treatment research that the existing method of disposing of biomedical waste containing POP through incineration is highly problematic and detrimental to the environment (Navale et al., 2019). A more environmentally conscious and swift degradation approach for managing such biomedical-associated POP waste involved subjecting it to treatment with a 20% ammonium bicarbonate solution (20% w/v ABC). This process leads to the creation of harmless by-products, specifically ammonium sulphate and calcium carbonate, in the form of sludge. Ammonium sulphate is commonly utilized in agriculture as a chemical fertilizer, while calcium carbonate serves as an additive within the construction sector. This technique is cost-effective but also adds value by repurposing waste materials for beneficial applications. Hence, the use of a 20% ABC solution might aid in the disinfection of used POP biomedical waste generated from patient samples like burns, accidents, fractures, and dental problems (Navale et al., 2019).

The summary of the different POP recycling methods in the industry is listed in Table 1.

Table 1.

Methods of POP recycling in industries

Industry	Method of Recycling
Building Construction Industry	Calcining POP waste collected at temperatures 150 to 200 °C for at least 24 h to create recycled POP
Ceramic Industry	Sintering POP waste at higher temperatures to create recycled POP filler Calcining at 180 °C to make recycled POP
Medical Industry	Treating POP bio-medical waste using 20% ammonium bicarbonate solution to get harmless by-products

2.2 Factors affecting recycling of POP.

2.2.1 Impact of Calcination Temperature and Time

Waste POP calcination temperature affects the properties of recycled POP. According to the study by De Moraes et al. (2016), temperature must be maintained in the range of 150^0C for three hours to get the maximum strength of the recycled POP(De Moraes Rossetto et al., 2016). In another study, the use of a calcination temperature of 148.5^0C for 2.22 h resulted in recycled POP with a compressive strength of 5.7MPa (Matani, 2017). A study carried out by Lokuliyana et al. (1988) used different temperatures in the calcination process (140-500^0C). Their results showed a similar presence of hemihydrate at temperatures 140 and 180^0C while with the increased temperature above 350 ^{0}C, β-POP could become inactive anhydrite, lowering the quality of produced POP. This shows that excessive temperatures can lead to over-calcination, and it could also lower the quality of the product (Lokuliyana et al., 1988). Similar results were obtained in another study confirming that the higher calcination temperature leads to decrease in compressive strength (De Moraes Rossetto et al., 2016).

Other than the temperature, calcination time duration could also affect the properties of recycled POP. The time duration for the recycling process of POP could vary from 1 to 24 hours; increasing the time duration for a fixed temperature resulted in an increase in compressive strength and surface hardness. According to the study, calcining the product at 150^0C for different durations resulted in recycled POP with low workability, higher surface hardness, and higher compressive strength than the original gypsum plaster (De Moraes Rossetto et al., 2016).

2.2.2 Particle size

According to the literature, the effectiveness and calibre of the recycling process are substantially affected by the impact of particle size on discarded POP. The rate of total calcination, reaction kinetics, and heat transmission are all significantly influenced by the particle size of the waste material. Larger surface areas are typically found in smaller particle sizes, which speeds up heat transportation and reaction kinetics during calcination. This may lead to more effective water removal from the crystallization process and the transformation of used POP into recycled POP. Larger particle sizes, on the other hand, can have slower heat transfer and insufficient calcination because of their decreased surface area and greater diffusion distances. In earlier studies, particle size was chosen as 36-300 μm in the production of recycled POP pastes (Badarulzaman et al., 2015; Geraldo et al., 2017; Jikan et al., 2013; Lokuliyana et al., 1988)

2.2.3 Sample size used for calcining

The effectiveness and precision of the recycling process are significantly impacted by the effect sample size used for calcination of waste POP. Heat distribution, reaction kinetics, and the uniformity of the calcination process are all directly impacted by sample size. Larger sample sizes may result in uneven heat distribution and slower heat penetration, which may compromise calcination and affect the plaster's quality. In contrast, smaller sample sizes might heat up more quickly and with better evenly distributed temperature, allowing for a thorough and regular conversion of used POP to recycled POP. To guarantee that the calcination process is both efficient and effective and produces high-quality plaster while consuming the least amount of energy and time period, it is imperative to reach the ideal sample size (Duan et al., 2022).

4.4 Plaster to water ratio

Usually, when creating a plaster, POP powder is added to the water. Various waste POP to water ratios have been used in the literature. An adequate amount of water in plaster ratio is directly involved in the strength of the resulting POP. In addition to the plaster-to-water ratio, mixing of the samples should be done carefully to avoid air bubbles. Overmixing will cause the plaster to set up quickly (lower setting time) before it can be poured into the mould (Matani, 2017). In another study of recycling POP, the plaster to water ratio was taken as 1:1, which gives an average compressive strength of 1028 KN/m^2 while the use of a 3:2 ratio produced recycled POP with an average compressive strength of 798 KN/m^2, emphasizing the detrimental effect higher water amount on compressive strength. The plaster water ratio of 100:75 was also reported in some studies (Matani, 2017).

2.2.5 Secondary materials to change the properties of POP

reused POP moulds quickly weaken, with their strength decreasing after each reuse. The addition of 25% (wt) of aluminium oxide as a retarder to the recycled plaster could increase the compressive strength as well as flexural strength in recalcination cycles. X-ray images of the moulds reveal larger gypsum particles as strength diminishes. Adding around 25% aluminium oxide significantly boosts strength and reduces particle size. This could be useful in places like die-casting factories, where moulds are disposable after a single use (Chemistry, 1926; Maciej Serda et al., 2013). Another study has revealed that sodium polyphosphate (STPP) could increase the water demand and delayed the hydration of recycled POP (setting time). STPP also provided hardened recycled POP with a loose structure, which led to lower strength and higher water absorption than recycled POP without STPP (Li et al., 2017).

Summary and perspective

According to previous studies on the recycling of POP, calcination temperature and time, particle and sample size used, and POP to water ratio play major roles in the final properties. The best calcination temperature can be identified as 180˚C with two hours time duration. By considering the particle size and practical scenario, a mesh size of 125-500 μm would be ideal for recycling of POP. The sample size needs to be carefully selected with the furnace used to optimise the heat transfer. POP to water ratio should be maintained at 1:1 to get the best compressive strength. A plaster-to-water ratio of 2:3 can also be used if the products do not need much strength and require lightweight, such as orthopaedics bandages, dental moulds, orthotics, etc. To control the strength reduction due to the calcining cycles of the POP, aluminium oxide can be selected as the secondary material to control the mechanical properties of recycled POP. Various chemicals (i.e., ABC) can also be used in the case of recycling discarded medical POP.

From the study, it is evident that used POP can easily be recycled and reused for same or multiple purposes. Despite all these findings, the recycling percentages of POP are very poor. This may be due to the presence of impurities in used POP, cheaper and easy access to raw POP, the need of secondary processing prior to recycling of used POP, poor awareness as well as irresponsibility on social and corporate duties. Thus, a systematic and commanding effort is needed to improve the recycling percentages of POP which consequently encourage the circular economy and sustainability.

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