Waste anthropogenic minerals in the circular economy

A Cieplińska¹, A Szymanek¹
¹Czestochowa University of Technology, Faculty of Mechanical Engineering and Computer Science, Institute of Thermal Machinery, al. Armii Krajowej 21, 42-201 Czestochowa, Poland

*acieplinska@imc.pcz.pl

Abstract. The article presents the possibility of using calcareous wastes to produce alternative sorbents for flue gas desulphurization. Calcareous wastes from chemical plants produced during the propylene oxide production process were used. In order to assess the potential of stored waste, they were subjected to comprehensive physical and chemical tests: the chemical, morphological, structural, fractional composition and reactivity were determined. Due to the nature of its formation, lime waste was subjected to electromagnetic activation to improve its sorption properties. The impact of activation on physico-chemical properties was also determined. The verification of the tests carried out on a micro scale was the flue gas desulphurisation test performed on a real object using the activation technology in an electromagnetic mill. The aim of the test was to obtain similar results of flue gas desulphurisation with the use of a waste sorbent for the lime milk used in this method.

1. Introduction
According to the definition, the circular economy (GOZ) is a concept aiming at the rational use of natural resources and limiting the negative environmental impact of manufactured products, which should remain in the economy as long as possible and the generation of waste should be minimized as much as possible [1]. It is a model of the economy that completely differs from the previously used, linear model, which was based on the assumption that resources are in large quantities, are easily obtainable and can be removed at a low cost. The increasing awareness that valuable resources are leaking from our economies in this way is taking steps to reuse them. One of the examples of circular economy is anthropogenic minerals derived from energy burning fossil fuels and biomass, called by-products of combustion, which are valorised in about 30%, and together with their use in reclamation - at the level of about 60% of the produced amounts [2]. Anthropogenic minerals are a huge base of alternative raw materials necessary in many industries. Considering the current legislative changes, the EU’s Raw Materials Initiative, and above all the assumptions of the Circular Economy that aim at maximum use of secondary raw materials, the definition of anthropogenic deposits should be extended to include raw materials from industrial processes [3,4]. The source of raw materials derived from such processes may be calcareous waste, which is a significant group of waste compounds, because it is estimated that about 1.5 million tonnes of high-calcium waste is generated annually in Poland. They are mainly found in the petrochemical, pharmaceutical, cosmetic, rubber, plastic and auxiliary industries. The most common calcareous wastes that are generated by the aforementioned branches of industry include: carbide residue, carbonate deposits from decarbonizing processes, brine purification deposit, and saponification and polyol and polyurethane production wastes. Post-production waste is usually directed to landfills for hazardous waste, finding no other way to use them. However, it is a source of limestone that can be utilized in various industries, primarily in the power industry, where significant amounts of fossil limestone are used to flue gas desulphurization, making it a potential recipient for recycled lime waste into anthropogenic sorbents.
2. The origin of waste generation and the concept of use
Lime waste used for the research was taken from the landfills of chemical plants producing polyols and polyurethanes. The most commonly used method in the industry for the production of propylene oxide is the chlorine method. The basic raw material used for its production is propylene, which when reacted with hypochlorous acid forms propylene chlorohydrin. In the technological process, calcium hydroxide is used in the form of milk for saponification of chlorohydrin. After changing the pH of chlorohydrin to strongly alkaline, it is removed as waste to a waste disposal site. Due to the specificity of its formation, the calcium hydroxide is chemically used and inactive with respect to the acid chemical components, thus it is not suitable for re-use.

Using the concept of circular economy, it was proposed to reuse stored waste in wet flue gas desulphurisation technology. The cycle began at the waste disposal site, the collected waste was subjected to mechanical activation in an electromagnetic mill to develop its reaction surface and restore chemical activity. The next step was to provide the activated material for the desulphurisation plant located on the site. In the chemical plant in question, the wet desulphurisation method is used, where calcium hydroxide is used as the sorbent, so it can be replaced with an alternative sorbent from waste. During the desulphurization process, flue gas comes into contact with the suspension and sulfur dioxide binds. The effect of desulphurization is not only the elimination of sulfur dioxide emissions, but also hydrated gypsum, which can be used in industrial and economic systems. For the concept outlined in this way, a research program was adopted, aimed at assessing the potential of stored waste and the possibility of its secondary use as a sorbent for flue gas desulphurization.

3. Research carried out and research methodology
The paper presents selected tests for examples of calcareous waste samples taken from landfills. Chemical, morphological, structural, fractional composition as well as reactivity of waste deposited in landfills was determined. The analysis of the granulometric composition and content of selected elements was performed by the SEM-EDX method. The waste structure was examined using a SEM scanning electron microscope manufactured by LEO Electron Microscopy LEO 1430VP, additionally equipped with an EDX Quantax 200 X-ray spectrometer with a Bruker AXS XFlash 4010 detector. The volume distribution of particle size was tested in the range of 0.01 to 2000μm, using the phenomenon of laser light diffraction using a MasterSizer 2000 apparatus from Malvern Instruments. To assess the sorption properties of the tested samples, reactivity tests carried out in accordance with the Ahlstrom Pyropywer-Reactivity guidelines were used. The reactivity index was determined from the Ahlstrom test, which involved sulphuring the samples under model conditions. The chemical analysis determined the contents of elemental calcium, carbon and sulphur prior to the test, and the content of sulphur after the sample sulphuring test. The Ca/S molar ratio, which takes account of the Ca content before the test and the sulphur content after the test, is called the reactivity index, \( R_i \) [kmol / kmol]. For the assessment of the sorption properties, the reactivity scale shown in Table 1 [5,6].

| Limestone Assessment | RI   | CI   |
|----------------------|------|------|
| excellent            | < 2.5| > 120 |
| very good            | 2.5 - 3.0 | 100 - 120 |
| good                 | 3.0 - 4.0 | 80 - 100 |
| sufficient           | 4.0 - 5.0 | 60 - 80 |
| poor                 | > 5.0 | < 60  |
The next stage of the research was to activate the analyzed samples to restore sorption properties. The main effect of the process is to increase the reaction surface of the activated waste, which increases as the grain diameter decreases. Mechanical activation was carried out in an electromagnetic mill, the process that occurs during its operation is mainly based on the principle of high frequency of chaotic collisions of ferromagnetic grinders with the material filling the working chamber in a rotating magnetic field [7].

4. Results and discussion

4.1. Laboratory scale research

4.1.1. Grain size and selected element contents analysis by the SEM-EDX method

The photographic documentation indicates high non-uniformity of the grain size, which spans the range of 0-300 µm. Figure 1 represent photograph of calcareous waste taken with a scanning electron microscope (SEM). Figure 2 shows an example EDX X-ray spectrometer spectrum with the detailed characteristic elements. Juxtaposing the data from the both devices enabled the determination of the percentage mass fraction of the regions analyzed, which is presented in Table 2.

![Figure 1. 2000 times magnification](image1)

![Figure 2. The X-ray spectrum from spectrometer EDX](image2)

| Sample number and sampling depth [m] | Percentage mass share of elements [%] |
|--------------------------------------|-------------------------------------|
|                                      | C  | O  | Mg | Al | Si | S  | Cl | Ca | Fe | Cu |
| I                                    | 0  | 9.04 | 46.92 | 2.54 | 0.60 | 0.77 | -  | 3.19 | 34.44 | 2.50 | - |
| I                                    | 0.5-1 | 11.51 | 39.09 | 1.09 | 1.01 | 0.39 | 0.01 | 4.26 | 33.25 | 9.24 | 0.15 |
| III                                  | 0  | 11.72 | 43.83 | 0.24 | 0.78 | 0.21 | -  | 6.10 | 36.73 | 0.40 | - |
| III                                  | 0.5-1 | 14.36 | 45.77 | 0.95 | 0.65 | 0.78 | -  | 4.65 | 31.47 | 1.35 | - |

Analyzing the data from Table 2, it can be seen that calcium constitutes 36.73%, it comes from calcium hydroxide, which is the basis of the examined waste. Noteworthy is the fact that the carbon content is high, which can be derived from the reaction of calcium hydroxide with CO2 contained in atmospheric...
air, as a result of which secondary carbonization of Ca (OH) 2 took place. The chlorine content, however, was 6.10% due to the use of chlorohydrin in the reactor during the saponification process.

4.1.2. Grain size distribution and specific area measurements on the Malvern grain size distribution analyser.

The waste deposited on the waste disposal grounds would undergo the process of secondary carbonization by attaching carbon dioxide from the atmospheric air; this phenomenon was also accompanied by an agglomeration phenomenon resulting in deposited material particles lumping together. Table 3 shows the results of the tests carried out on the sample not activated in the electromagnetic mill.

**Table 3. Particle size distribution and surface area of lime waste before activation.**

| Sample number and sampling depth [m] | Specific Surface area [m²/g] | Surface weighted mean D[3,2] [µm] | Volume weighted mean D[4,3] [µm] | d (0,1) [µm] | d (0,5) [µm] | d (0,9) [µm] |
|-------------------------------------|-------------------------------|---------------------------------|---------------------------------|--------------|--------------|--------------|
| I                                   | 0                            | 11,602                          | 120,975                         | 6,201        | 39,853       | 402,611      |
|                                       | 0.5-1                        | 0,545                           | 11,014                          | 6,115        | 35,799       | 372,150      |
| III                                 | 0                            | 11,475                          | 124,581                         | 6,233        | 37,934       | 397,217      |
|                                       | 0.5-1                        | 0,491                           | 12,493                          | 6,621        | 44,547       | 498,871      |

In order to break up the agglomerates formed and increase the sorption surface of the tested waste, electromagnetic activation was used, and the results of the measurements are given in Table 4.

**Table 4. Particle size distribution and surface area of lime waste after activation.**

| Sample number and sampling depth [m] | Specific Surface area [m²/g] | Surface weighted mean D[3,2] [µm] | Volume weighted mean D[4,3] [µm] | d (0,1) [µm] | d (0,5) [µm] | d (0,9) [µm] |
|-------------------------------------|-------------------------------|---------------------------------|---------------------------------|--------------|--------------|--------------|
| I                                   | 0                            | 4,156                           | 8,647                           | 2,606        | 7,079        | 15,459       |
|                                       | 0.5-1                        | 1,46                            | 4,115                           | 2,588        | 7,013        | 15,209       |
| III                                 | 0                            | 3,792                           | 10                              | 2,291        | 6,581        | 15,382       |
|                                       | 0.5-1                        | 1,49                            | 3,843                           | 2,316        | 6,615        | 15,401       |

Based on the data contained in Tables 3 and 4, we can conclude that as a result of using the activation, the specific surface area in the tested material increased from 0.491 to 1.54 [m² / g]. We also see a significant decrease in the average grain diameter after activation from 12.493 to 3.792 [µm] (D [3.2]) and from 158.911 to 8.633 [µm] (D [4.3]). Noteworthy is the fact that after activation all samples had the same grain distribution regardless of the grain distribution of the initial material. It can therefore be concluded that electromagnetic activation has led to an increase in the reaction surface and also increased their chemical activity.
4.1.3. Ahlstrom reactivity studies

Ahlstrom reactivity tests were used to assess sorption properties. The reactivity index $R_i$ was tested. Table 5 presents the results of the waste material testing before and after activation and the increase in reactivity.

Table 5. The results of tests on the reactivity of lime waste before and after electromagnetic activation and the increase in reactivity after activation.

| Sample number and sampling depth [m] | Distance from the edge of the landfill [m] | Reactivity before activation | Reactivity after activation | Increase of reactivity after activation $\Delta R_i$ [%] |
|-------------------------------------|------------------------------------------|----------------------------|----------------------------|-----------------------------------------------|
| I                                   | 0                                        | 4.93                       | 3.60                       | 26.99                                         |
|                                     | 0.5-1                                     | 4.11                       | 2.59                       | 37.05                                         |
| III                                 | 0                                        | 4.71                       | 2.87                       | 39.06                                         |
|                                     | 0.5-1                                     | 4.01                       | 2.64                       | 34.16                                         |

From the collected results presented in Table 5 and the scale of reactivity from Table 1, it can be found that the rate of the tested waste ranged from 3.72 to 5.12 before the activation process, which means that the tested material without any treatment was distinguished by the features of sorbents good and sufficient quality. The obtained test results confirmed that the analyzed product is chemically used and does not react with acidic components. Whereas subjected to activation, it was characterized by a discrepancy in the sorbent class range, and the reactivity index after activation ranged from 2.59 to 3.60. This means that the tested treated material was characterized by very good quality sorbents. The obtained results indicate the high sorption potential of the tested samples and the possibility of using it in flue gas desulphurization.

4.1.4. Summary of the results of the analyzes carried out

After conducting a series of physicochemical tests aimed at determining the potential of stored waste, an analysis of their suitability for use in the wet method of flue gas desulphurization was carried out. The material was characterized by a high calcium content and was present both in the form of agglomerates and individual particles, inactive in relation to acidic chemical components. The use of electromagnetic activation caused a number of physicochemical changes in activated materials, i.e. the breakdown of agglomerates, micronization and alignment of the granulation as well as the increase in the specific surface, which is the reaction surface of the tested waste. This technology makes it possible to obtain a full-value sorbent for the flue gas desulphurisation method.

4.2. Industrial research

The verification of the results obtained on a laboratory scale was the testing of flue gas desulphurization with activated lime waste on a real object. The aim of the test was to obtain approximate results of flue gas desulphurisation for the standard lime milk method used in the wet method. The test was carried out in two stages, the first one involved collecting process data of flue gas desulphurization using classic calcium hydroxide in order to create a comparative base for proper tests. In the second stage of the test, an electromagnetic mill was installed next to intermediate whitewash tank in the flue gas desulphurization installation. The waste from the landfill was dosed to the mill, then the activated material went to the intermediate tank and then to the scrubber. An industrial test was carried out using a classic sorbent in the form of Ca (OH) 2 used as a comparative base (figure 3), and then a specific test was carried out for the tested alternative waste sorbent (figure 4).
The test showed that the desulphurisation efficiency ($\eta_{sr}$) was obtained with a classic sorbent at 70.72%, while for the activated sorbent this value clearly increased to 77.81%. In addition, the consumption of activated waste sorbent during the tests was lower by approx. 25% than with the use of calcium hydroxide.

5. Conclusions
According to the analysis carried out on a micro scale and tests carried out on an industrial scale, the activation technology in an electromagnetic mill enables the transformation of stored limestone waste into a high-quality alternative substitute for sorbents obtained from natural resources. Reusing waste has many ecological and economic benefits, such as reducing SO$_2$ emissions, reducing the consumption of natural resources, reducing the number of landfills, and reducing storage fees. Additionally, as a result of the reaction of binding the activated limestone slurry with sulfur dioxide during the wet flue gas desulphurisation process, hydrated gypsum is formed, which can practically be used in systems of economic and industrial use. Bearing in mind the current legal regulations and the assumptions of the Circular Economy, the EU's Raw Materials Initiative, which provide for the maximum use of secondary raw materials, the term anthropogenic deposits should be extended to include raw materials resulting from industrial processes.

Acknowledgements
Publication supported financially under Contract No. 944/P-DUN/2019 from funds of MNiSW intended for the dissemination of science (DUN).
This research was supported by project „Technological Initiative I” „Sorbents from waste” KB/142/13292/IT1- B/U/08.

References
[1] Programy i projekty. Gospodarka o obiegu zamkniętym, dostępne na stronach internetowych Ministerstwa Środowiska, dostęp dnia 21.08.2019
[2] Szczygielski T 2015 *Minerały antropogeniczne a gospodarka o obiegu zamkniętym* (Warszawa: Politechnika Warszawska)
[3] Szczygielska D 2015 Wykorzystanie mineralów antropogenicznych w gospodarce o obiegu zamkniętym *Minerały antropogeniczne a gospodarka o obiegu zamkniętym* ed T Szczygielski (Warszawa: Politechnika Warszawska) pp 17-29
[4] Szczygielski T, Masłowska D 2017 Przyczynki do systematyki zasobów antropogenicznych XXIV Międzynarodowa Konferencja Popioły z Energetyki pp 1-15
[5] Wytyczne Ahlstrom Pyropower-Reactivity index 1995 (Ahlstrom Pyropower)
[6] Szymanek A, Nowak W 2007 Mechanically activated limestone *Chem. Processs. Eng.* 287 pp 127-137
[7] Szymanek A 2006 Mechaniczno-chemiczna aktywacja kamienia 8 Konferencja Osiągnięcia w Nauce, Energetyce i Przemyśle POL-EMIS 2006 pp 211-214