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AN INNOVATIVE METHOD OF ACTIVATING LIME WASTE. WASTE – SORBENT - PRODUCT

Abstract
The paper presents the production technology of sorbents for flue gas desulphurization with the wet limestone method, produced on the basis of limestone waste. The waste was subjected to comprehensive physicochemical tests and the following were studied: size distribution, chemical composition, morphology and reactivity. The analysed waste was subjected to electromagnetic activation to improve the sorption properties lost in the original process. The effect of the activation process was determined by comparing physicochemical properties of the waste before and after its activation. Based on the experience gained, an industrial installation was designed and manufactured industrial.

Key words
Limestone waste, electromagnetic mill, activation, sorbent, desulphurization.

Introduction

Calcareous wastes represent a significant group of waste compounds. It is estimated that in Poland about 1.5 million tonnes of waste is formed with a high calcium content. Such large amounts of waste of this type may constitute a source of calcium compounds for various industries. The industry that uses the large amounts of fossil limestone for flue gas desulphurisation is the energy industry. This branch of industry can become a potential recipient respectively of processed waste calcium compounds, especially given that a large increase in the demand for lime sorbents is expected as a result of the introduction of further emission limits. The introduction in Poland of the provisions of Directive 2010/75 / EU (IED) and the guidelines concerning the best available techniques (BAT) will tighten the sulfur dioxide emission requirements. This will particularly affect smaller installations that usually do not have a flue gas desulfurization system. For example, after a transitional period: for emitters in the range up to 100 MW, the emission limit value will fall from 1500 to 150 - 360 mg/Nm^3, while from 100 to 225 MW it will fall from 1500 to 80 - 200 mg/Nm^3[1][2]. Tightening the emission limit values for sulphur dioxide emissions means that their value will be several times smaller than at present. The necessity of such a large reduction in SO_2 emissions will cause a rapid increase in the demand for limestone in various forms, used for various methods of flue gas desulphurisation. Exploitation of the potential of waste calcium compounds would allow to partial meeting of the increase in demand for SO_2 sorbents caused by the new requirements and to protect natural limestone deposits. An example of waste that could meet the conditions for what are the limestones used in the desulfurization of flue gas, could be the calcium waste formed in the process of producing propylene oxide.

Materials and methods

The waste calcium compounds used for the study were taken from chemical plants using calcium hydroxide in the process of producing propylene oxide. These wastes arise in the chlorochridrone saponification process using calcium hydroxide and are in the form of a low-concentrated solution (0.3-0.4%) of $Ca(OH)_2$. A schematic diagram of the process of forming the analysed waste is shown in Figure 1. The waste produced in the presented process occurs in the form of: a filter cake directly from production and waste deposited in landfills.

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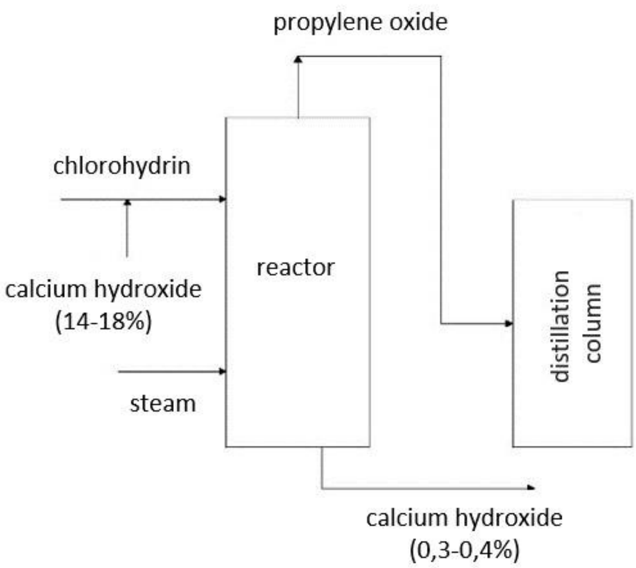


Fig. 1. The production process of propylene oxide
Source: Author's

The material for tests was taken both from the filter cake straight from the production, as well as from landfills on which the waste was deposited over a long period of time. For samples taken a series of physical and chemical analyses were made. The following parameters were analysed: moisture content, chemical composition, heavy metal content, granulometric composition and sorptive properties with respect to SO_2. Moisture content was determined according to PN-76/B04350 standard at 105^{o}C, chemical composition analysis was performed according to the PN-EN I96-2;1996 standard, whereas heavy metals were determined by ASA method according to the PN-ISO 8288;2002. Investigations of the granulometric composition of waste were made using the Mastersizer 2000 laser granulometer manufactured by Malvern Instruments Ltd. with a particle size range from 0.01 to 2000 µm. The value of the specific surface area was determined using the Blaine method. The tests of sorption properties were carried out, determining: the reactivity index Ri, the absolute sorption Ci and the conversion rate X for the dry mass of the waste. The reactivity index and absolute sorption were determined in accordance with the Alsthrom Propywe-Reactivity guidelines. The reactivity index were defined as the Ca/S molar ratio, which takes into account the Ca content before the test and the S content after the test. The absolute sorption index Ci is defined as the mass of sulfur [g] absorbed by the kilogram of the sorbent under test. The conversion rate was defined as the amount of moles of Ca that had reacted to $CaSO_4$ [3,4,5,6].

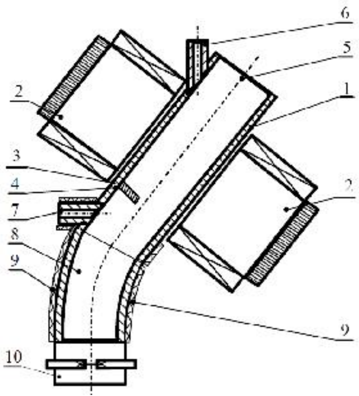
Experimental procedure

In the first stage of the research, waste samples were subjected to initial physicochemical analysis, determining their: moisture content, chemical composition, heavy metal content, granulometric composition and sorptive properties with respect to SO_2. In the next stage of the research, the samples were subjected to the activation process. For the activation of the calcium waste, an electromagnetic mill is used. The process of waste activation took the following course: the calcium waste from the feed tank was fed through the pump to the working chamber of the mill. In the working chamber, the material was subjected to mechanical treatment by rotating grinding media (grinding time about 10 sec) as well as the operation of a strong electromagnetic field (magnetic induction 1,2 T). In the working chamber the material was subjected to the action of chaotically rotating fine grinding elements which, acting on the feed, break down agglomerates and cracking and crushing of its grains. The product obtained after the activation process was gravitationally discharged into the product container.

The basic effect of the activation process is to increase the specific surface area of the activated waste particles. This surface increases as the diameter of the particles decreases, which translates into improved sulfur dioxide bonding properties. The specific surface of the particle is thus the surface of the reaction. Another way to increase the reaction surface in the area of the same fraction of particles is to develop their surface structure. A large number of small grinding elements and a high frequency of impacts on waste grains enable the crushing of the grain surface, increasing gaps and pores. After the activation, the sorption properties and granulometric composition were again determined using the same test procedures. The process of waste activation was carried out according to the patent "The method of sorbent preparation for the wet flue gas desulfurization process" [7].

Electromagnetic mill

An electromagnetic mill is a device that uses the phenomenon of a rotating magnetic field, under the influence of which small ferromagnetic grinding elements move chaotically inside the working chamber of the mill. The mill, as the main element of the electromagnetic activator installation, consists of two main parts: a grinding chamber with grinding elements and a stator with six windings. The grinding chamber is a non-ferromagnetic tube inside which small, ferromagnetic grinding elements move in the rotating magnetic field. The whole is a working area in which the material is subjected to mechanical, thermal and magnetic field treatment. With the increase of the magnetic induction value inside the working chamber, small grinding elements are introduced into an increasingly turbulent motion. The ferromagnetic grinder, under the influence of magnetic field induction, becomes a magnetic dipole with specific poles, attracted by this field with a specific force. Due to the small size and the appropriate shape and proportions of the dimensions, it is possible to achieve high acceleration and quickly achieve the maximum speed of grinder [8]. In connection with the very fast rotational movement of grinding media, the number of strokes of grinding elements per particles of activated waste is also significant. In addition, the grinding media working under the influence of magnetic induction and mutual collisions heat up, transfer heat to the substrate. A diagram of the construction of the electromagnetic activator and the view of the electromagnetic field exciter are shown in Figure 2. Use of the mill waste activation in the patent describes the electromagnetic "Device to activate the sorbents" [9].



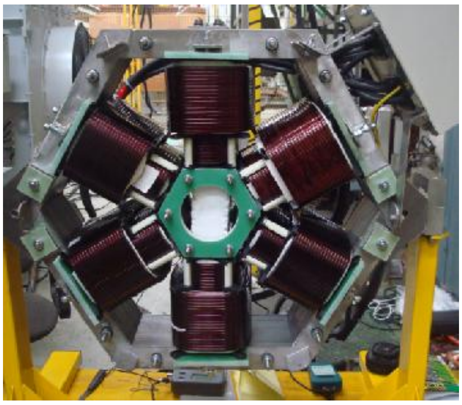


Fig. 2. Diagram of the construction of the electromagnetic activator (left). Description: 1 - working chamber, 2 - inductor poles, 3 - winding, 4-aperture grinding elements, 5 - charging hole, 6 - inlet hole, 7 - measuring force, 8 - product receiving segment, 9 - thermal insulation, 10 - connector for tight connection with the product receiving container and the physical model of the inductor (right).

Source: Author's

Results analysis

Research humidity showed a level of over 70% of its contents in the samples from landfills. Research on waste after production as a "filter cake" showed a moisture content at a level of 40%. The results of analyses of the chemical composition of waste are shown in Table 1, and the results of tests for heavy metals in Table 2.

Table 1. Average chemical composition of the tested samples (dry mass) [%].

No.	Component	Waste from the landfill		Filter cake	
		Mean values	Standard deviation	Mean values	Standard deviation
1	SiO_2	3.50	0.05	3.20	0.06
2	Fe_2O_3	1.20	0.02	0.98	0.02
3	Al_2O_3	1.75	0.01	1.73	0.05
4	CaO	49.4	1.20	51.2	1.43
5	MgO	2.24	0.24	2.27	0.21
6	SO_3	0.60	0.02	0.71	0.03
7	Ignition losses	31.4	1.58	27.6	1.87

Source: Author's

Table 2. Heavy metals content (dry mass) [mg/kg].

No.	Component	Waste from the landfill		Filter cake	
		Mean values	Standard deviation	Mean values	Standard deviation
1	Copper	0.003	0.0002	0.003	0.0003
2	Nickel	0.012	0.0007	0.013	0.007
3	Zinc	0.03	0.005	0.025	0.005
4	Chrome	0.001	0.0002	0.001	0.0003
5	Cadmium	0.001	0.0002	0.001	0.0002
6	Manganese	0.056	0.0005	0.053	0.0006
7	Lead	0.12	0.005	0.13	0.004

Source: Author's

In test samples about 50% of the content of calcium was found. In the waste from the landfill, 70% of it was calcium carbonate, the remaining part being calcium hydroxide and calcium oxide. In the case of the filter cake, more than 90% was calcium hydroxide. The tests of sorption properties were carried out, determining: the reactivity index Ri, the absolute sorption Ci and the conversion rate X for the dry mass of the waste. The results of the analyses carried out are presented in Table 3. Samples 1, 2 and 3 correspond to averaged sample taken from different landfills.

Table. 3. Results for reactivity indices

Sample	Parameters					
	R_i [mol/mol]		C_i [g/S kg]		X [%]	
	Mean values	Standard deviation	Mean values	Standard deviation	Mean values	Standard deviation
1	3.88	0.29	81	5.12	26	2.65
2	4.07	0.38	75	4.38	24	1.21
3	4.0	0.41	78	4.21	25	2.05
Filter cake	3.55	0.46	97	5.39	29	0.98

Source: Author's

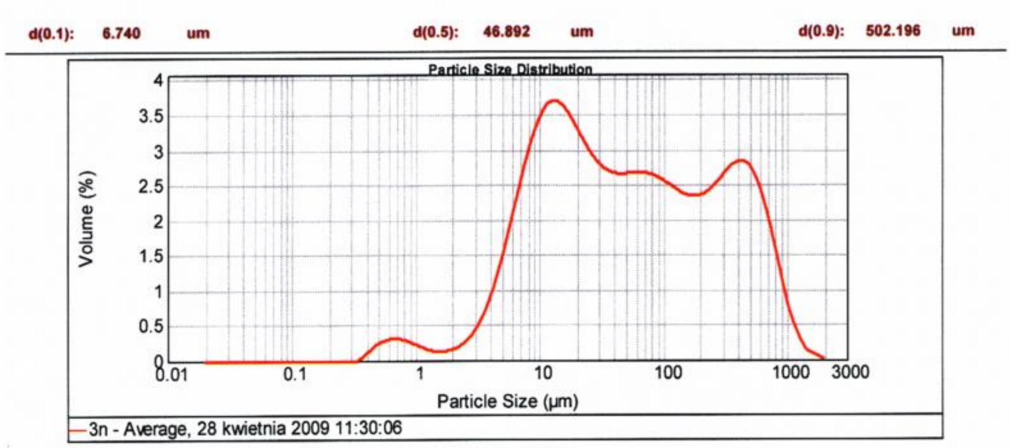
Before activating the reactivity rates were within the limits (3.55-4.07), according to the Alhstrom classification (Table 4), the waste calcium compounds were in a sufficient and good class.

Table 4. Scale of reactivity of sorbents

Evaluation of limestone	R_i	C_i
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
Low quality	> 5.0	< 60

Source: [5,6]

Studies regarding the granulometric composition of waste were made using the Mastersizer 2000 laser granulometer manufactured by Malvern Instruments Ltd. with a particle size range from 0.01 to 2000 µm. The figure below presents an example of the analysis of the particle distribution of waste from landfill.



Size (µm)	Volume In %
0.020	44.89
35.000	4.39
45.000	8.91
75.000	4.93
100.000	

Size (µm)	Volume In %
100.000	10.93
200.000	6.56
300.000	9.31
500.000	8.85
1000.000	

Size (µm)	Volume In %
1000.000	1.23
2000.000	

Fig. 3. Particle size distribution waste collected from the landfill.
Source: Author's

The particle distribution of the waste was in the range of 0.02 to 2000 µm, with the advantage of the grains in the range of 0.02 to 35µm (ca. 45%). The average diameter of grains was in the range 35.89 - 46.89 µm, while the surface area ranged from 0.474 to 0.545 m^2/g, the standard deviation was 0,04 m^2/g

The results of the research have confirmed that the waste calcium compounds after the production of propylene oxide show favourable physico-chemical properties, predisposing them for use as sorbents of sulfur dioxide. However, due to the decreased reactivity and unfavourable sorbent injection process, the particle size distribution requires proper pre-treatment (activation).

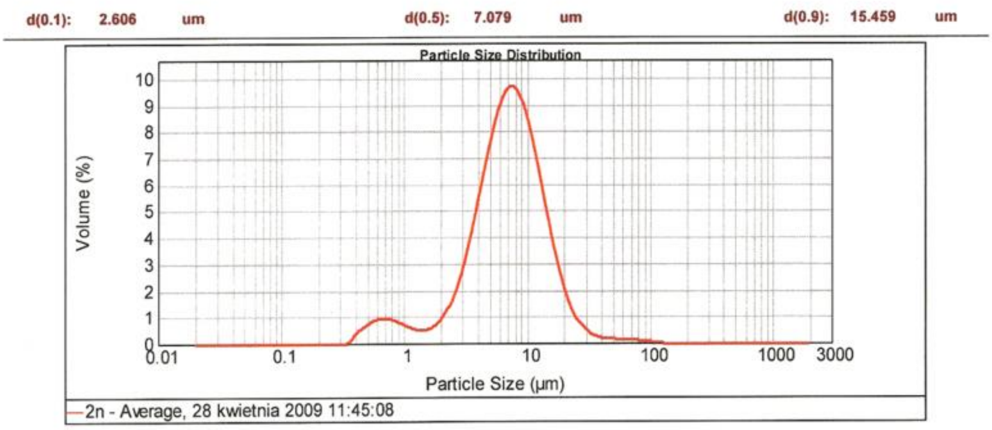
After the activation, the sorption properties and granulometric composition were again determined using the same test procedures as in the initial tests. Table 5 and Figure 4 present examples of results of investigations of activated waste.

Tab. 5. Results for reactivity indices samples after activation

Sample	Parameters					
	Ri [mol/mol]		Ci [g/S kg]		X [%]	
	Mean values	**Standard deviation**	**Mean values**	**Standard deviation**	**Mean values**	**Standard deviation**
1	2.91	0.39	101.25	6,18	34	1.68
2	2.89	0.43	97.50	4.83	35	2.73
3	2.76	0.52	102.18	5,27	36	2.79
cake filter	2.65	0.41	109.30	6.39	39	1.43
calcium hydroxide	2.23	0,38	129.00	5.49	45	1,05

Source: Author's

After activation, reactivity ratios reached a value of 2.65 - 2.91 and accordance with the Alhstrom's classification (table 4) were in the class, very good. Particle distribution of the waste was in the range of 0.02 to 100 µm, with the majority of the grains in the range of 0.02 to 35µm (ca. 98%). The average diameter of grains was in the range 6.09 - 7.09 µm. While the specific surface area ranged from 1.44 to 1.54 m^2/g, the standard deviation was 0.05 m^2/g.



Size (µm)	Volume In %
0.020	
35.000	98.91
45.000	0.36
75.000	0.50
100.000	0.17

Size (µm)	Volume In %
100.000	
200.000	0.05
300.000	0.00
500.000	0.00
1000.000	0.00

Size (µm)	Volume In %
1000.000	
2000.000	0.00

Fig. 4. Particle size distribution samples after activation.
Source: Author's

Summary of the analysis results

When comparing the results of the analysis of lime waste before and after the activation process, we can see a significant improvement in the parameters relevant for the SO_2 sorption process. Analysing the particle size distribution of waste, we can see that it was characterized by the following data: specific surface area 0.474 - 0.545 m^2/g, before activation and 1.44 - 1.54 m^2/g after activation. Activation allowed for the development of a specific surface area of 300%. The average diameter of grains decreased from the horizontal 35.89 - 46.89 µm, before activation to 6.09 - 7.09 µm after activation. The value of the reactivity index before activation fluctuated in the range from 3.55 to 4.07 (sufficient and good class). After the activation process, the reactivity rates ranged from 2.65 to 2.91 which classifies them as very good. In all cases, there has been an increase in sorption properties, which ranged from 33 to 44%. Despite activation, it was not possible to achieve reactivity as for pure calcium hydroxide. The result was lower by 18 to 30%.

The obtained results of analyses indicate, that waste calcium compounds subjected to activation in an electromagnetic mill can be used as a full-value sorbent in the wet flue gas desulfurization method. Confirmation of the possibility of using the potential of lime waste as a sorbent was achieved. It allowed to carrying out of design works, as a result of which was an industrial installation of limestone waste activation, using the electromagnetic mill technology.

Industrial research

To verify the results obtained and the correctness of the design of the devices, an industrial test of flue gas desulfurization with the use of activated waste was carried out. The test was divided into two parts. In the first part of the research, data were collected to create a comparative database. The process data for flue gas desulfurization using classical calcium hydroxide was collected. In the second part of the research, an electromagnetic mill was installed next to the intermediate tank of whitewash. The waste from landfills was delivered by car transport. Dosing to the mill was carried out using a pump and a flexible hose. The activated waste entered the intermediate tank and then the scrubber. Figure 5 shows the process of waste activation in industrial conditions.

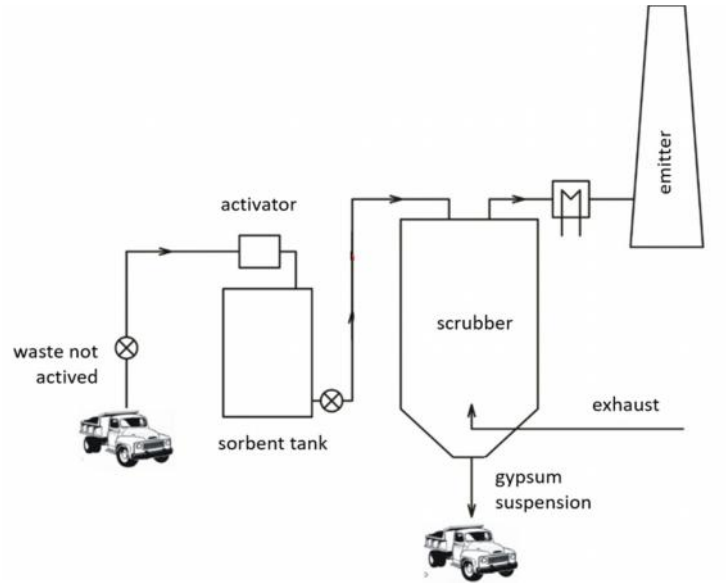


Fig.5. Process activation
Source: Author's

During the test, efficiency of flue gas desulphurisation was obtained at 77.81%, which was higher than the efficiency obtained in comparative studies (70.72%). In addition, the consumption of sorbent activated during the tests was lower by 25% than the consumption of calcium hydroxide, and thermal load boilers wavered within 5%. The obtained results were definitely better than earlier estimates. It was assumed that a comparable efficiency of flue gas desulphurisation would be obtained, but at about 20% increased stream of used waste in relation to calcium hydroxide. The results obtained from the industrial trial considerably surpassed expectations. A higher level of the efficiency of flue gas desulphurisation was obtained, with a 25% lower stream of activated sorbent, compared to the use of classical sorbent. In Figure 8, a view of the installation of waste limestone activation connected to a sorbent tank is shown.

Fig. 6. Installing the activator on the real object
Source: Author's

Summary
Increased consumption of calcium sorbents caused by successive tightening of SO_2 limits may become a stimulus for attempts to use waste calcium compounds, as sorbents in the different methods of flue gas desulfurization. As has been shown, this type of waste can become a full-value sorbent. Only the process to restore them to the original sorption properties lost in the processes of their original use is necessary. An example of such a process may be, as presented in the article, the process of activation based on the innovative technology of an electromagnetic mill. This technology makes it possible to transform stored waste in a technologically simple way so that it can be re-used. The reuse of waste as SO_2 sorbents brings a number of environmental and economic benefits.

- Strain off the environment by reducing the amount of waste deposited and the resulting savings associated with the costs of its storage.
- Savings associated with the lack of buying fossil limestone, and thus the protection of the natural deposits.

The use of waste sorbents in the wet flue gas desulfurization method allows us to connect the positive aspects of the liquidation of the landfilled waste, with simultaneous reduction of the sulfur oxides emitted into the atmosphere. As a final result, giving a commercial product which is synthetic gypsum. The results of trials of desulfurization and the benefits resulting from the application of the activated waste, enabled the industrial implementation of innovative lime waste activation technology.

Acknowledgements
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