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CONVERSION OF CALCIUM CARBONATE INTO SYNTHETIC GYPSUM IN FLUE GAS DESULPHURIZATION TECHNOLOGY USING WET LIMESTONE METHOD

KONWERSJA WĘGLANU WAPNIA DO GIPSU SYNTETYCZNEGO W TECHNOLOGII ODSIARCZANIA SPALIN ENERGETYCZNYCH MOKRĄ METODĄ WAPIENNĄ

Abstract

The paper presents application of calcium carbonate, which is included in the limestone, for wet limestone method of desulphurization used for flue gas generated in hard and brown coal combustion in pulverized coal furnaces of power boilers. Conversion stages of calcium carbonate into calcium sulphate dihydrate, i.e. synthetic gypsum, are given. Its physicochemical characterization and properties which cause it to resemble natural gypsum are specified. It was proved that the process of converting calcium carbonate into synthetic gypsum meets all the conditions justifying recognizing the process as one of environmental control methods known as recycling.

Keywords: flue gas desulphurization, limestone method, calcium carbonate, sorbent, recycling, synthetic gypsum

Streszczenie

W artykule omówiono zastosowanie zawartego w kamieniu wapiennym węglanu wapnia do odsiarczania mokrą metodą wapienną spalin energetycznych, powstających w procesie spalania węgla kamiennego i brunatnego w pyłowych paleniskach kotłowych. Podano etapy konwersji węglanu wapnia do dwuwodnego siarczanu wapnia, czyli gipsu syntetycznego. Podano jego charakterystykę fizykochemiczną oraz właściwości nadające mu cechy gipsu naturalnego. Wykazano, że proces konwersji węglanu wapnia do gipsu sztucznego spełnia wszystkie warunki upoważniające do stwierdzenia, że jest to jedna z metod ochrony środowiska naturalnego, zwana recyklingiem.

Słowa kluczowe: odsiarczanie spalin, metoda wapienna, węglan wapnia, sorbent, recykling, gips syntetyczny

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1. Introduction

Prior to deliberating whether the transformation, taking place in power industry flue gas desulphurization using wet limestone method, of a sorbent in the form of limestone and including over 95% of calcium carbonate, into synthetic gypsum has the hallmarks of recycling of expended substance into one of new properties, it would be necessary to define the notion of recycling.

Recycling is one of natural environment control methods. Its purpose is to limit the consumption of natural raw materials and to reduce the volume of wastes.

According to the Law on wastes of 27 April 2001 [1], recycling "is understood as such recovery which consists in repeat processing of substance or materials included in wastes by using production process in order to get substance or material of primary or other purpose, including also organic recycling, excluding recovery of energy".

The principle of recycling operation is to maximize the reuse of the same materials, taking into account minimization of expenditure for their processing, hence protected are natural resources used to fabricate these materials and raw materials used for further processing.

According to the Law on wastes [1], the power industry flue gas desulphurization technology using wet limestone method can be considered a method of natural environment protection because it meets the following recycling conditions:
– it reduces consumption of natural gypsum being one of natural resources,
– it reduces the volume of generated wastes in comparison with the volume of wastes created in flue gas desulphurization processes other than wet limestone method, the final product of which is the synthetic gypsum,
– it enables to recover the consumed sorbent (limestone) as a substance for a new purpose, namely the synthetic gypsum with properties not worse than those of natural gypsum.

2. Calcium carbonate characterization

Calcium carbonate ($CaCO_3$) is a white crystalline substance sparingly soluble in water. It is solubilised in water saturated with carbon dioxide (converting into calcium bicarbonate). At high temperature (in decarbonisation process) and under the action of acids, it is subjected to decomposition, causing carbon dioxide to be released and calcium oxide to be the final product of these processes.

Calcium carbonate is very common in nature. It is included in many minerals, e.g. calcite and aragonite [2] as well as dolomite, chalk and bark [3]. As limestone, it is used as a building stone, and after powdering – as a raw material in producing the burnt lime used to get hydrated lime. Calcium carbonate is used first and foremost in building industry, lime and cement production works, in chemical industry, sugar industry and metallurgy. In agriculture, it is a fertilizer while in power generation industry, it has been used as the cheapest sorbent in boiler flue gas desulphurization processes since the mid-20th century. Being the main component of limestone, calcium carbonate can be used in dry powdered form (dry method) or as a water slurry of milled limestone

(wet limestone method). The dry method (Furnace Sorbent Injection – FSI) consists in feeding the milled limestone, including over 90% $CaCO_3$, at granulation of about 100 μm, to the furnace chamber of pulverized-fuel boiler. There are three ways possible for feeding the sorbent into the boiler:

– it is directly mixed with coal (e.g. in a mill),
– it is blown into furnace chamber around the flame,
– it is blown into furnace chamber above the flame (preferred way).

A specific dry method of flue gas desulphurization is when coal is combusted in fluidized bed while powdered limestone, with granulation of about 1 nm, is simultaneously batched into the boiler furnace. The products of dry desulphurization (in FSI method these are: $CaSO_3$, $CaSO_4$, CaO, non-used sorbent and volatile ash) are seldom used in business practice. Products of flue gas desulphurization in fluidized bed boilers (non-used sorbent, volatile ash and $CaSO_4$) find a wider application.

3. Limestone characterization

One hundred and fifty million years ago, at late Jurassic period, most of the Polish territory was under warm sea spreading from the lands of present-day Russia on the East to the North Sea on the West. The conditions prevailing at that time contributed to the development of calcareous sedimentary rocks. They are now visible on ground surface over the area of Jura Krakowsko-Częstochowska, the Świętokrzystkie Mountains, the Tatra and Pieniny Mountains and at Western Pomerania (surroundings of Kamień Pomorski town), and in the Carpathians (Kruchel Wielki near Przemyśl) as large-size blocks of rock material, torn away from matrix substrate as a result of specific geological process.

Now, calcareous rocks, known as limestone, play an important role both in economy and in everyday life of people; since the mid of the previous century, due to a high content of calcium carbonate, they have become a common sorbent in desulphurization processes of power industry flue gases. In advanced technologies of flue gas desulphurization (e.g. in wet limestone method), limestone is subjected to transfer into synthetic gypsum, which is a desirable process due to the protection against sulphur dioxide atmospheric pollution.

Limestone to be used in flue gas desulphurization is tested for its size analysis and chemical constitution. An exemplary size analysis of dry milled limestone used in boiler flue gas desulphurization process in one of Polish power plants is given in Fig. 1. The size analysis illustrating fractions of particular particle sizes and their combined distribution was made using laser meter of particle sizes, the HELOS BR type manufactured by Sympatec. Determinations were also made for limestone density and specific surface of its particles. They are: $\rho = 2.710$ g/cm^3 and $S = 11.420$ cm²/g, respectively. The size analysis of sorbent influences the speed of dissolving the limestone particles in water and the pH value – the finer the particles, the higher the pH value.

In turn, the chemical composition of sorbent, a sample of which is presented in Tab. 1, influences its reactivity on contacting with SO_2 and contamination of the final product of flue gas desulphurization (synthetic gypsum) [4].

$x_{10} = 0.66$ μm $\quad\quad$ $x_{50} = 4.50$ μm $\quad\quad$ $x_{90} = 44.59$ μm $\quad\quad$ SMD = 1.94 μm $\quad$ VMD = 14.63 μm
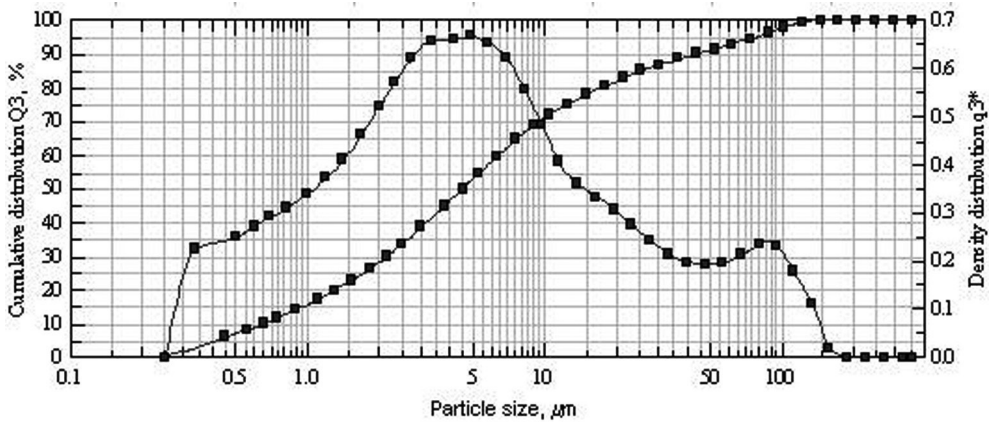
$x_{16} = 1.03$ μm $\quad\quad$ $x_{84} = 23.90$ μm $\quad\quad$ $x_{99} = 121.54$ μm $\quad\quad$ $S_V = 3.09$ m²/cm³ $\quad$ $S_m = 11419.63$ cm²/g

Fig. 1. Size analysis of milled limestone. $x_{10}…x_{99}$ – diameters of particles, whose combined fractions are less than 10…99% of the volume of all particles, SDM – average superficial diameter of particle set, VMD – average volumetric diameter of particle set, S_v – specific surface area of particles per unit of volume, S_m – specific surface area of particles per unit of mass, $q3* – q3$(log)

Rys. 1. Skład ziarnowy zmielonego wapienia. $x_{10}…x_{99}$ – średnice cząstek, których skumulowane udziały stanowią mniej niż 10…99% objętości wszystkich cząstek, SDM – średnia średnica powierzchniowa zbioru cząstek, VMD – średnia średnica objętościowa zbioru cząstek, S_v – powierzchnia właściwa cząstek odniesiona do ich objętości, S_m – powierzchnia właściwa cząstek odniesiona do ich masy, $q3* – q3$(log)

Table 1

Physical and chemical characterization of limestone dust

Component, process parameter	Unit	Process boundary value
$CaCO_3$	[% by wt.]	≥ 95.00
MgO	[% by wt.]	≤ 1.00
$NR+SiO_2$	[% by wt.]	≤ 2.50
SiO_2	[% by wt.]	≤ 2.00
Fe_2O_3	[% by wt.]	≤ 0.50
Al_2O_3	[% by wt.]	≤ 0.50
SO_3	[% by wt.]	≤ 0.30
Na_2O	[% by wt.]	< 0.05
K_2O	[% by wt.]	< 0.05
Humidity	[% by wt.]	≤ 0.50
OWO (TOC)	[Mg/kg]	≤ 0.20
Temperature	[°C]	$(-30.0) \div (+35.0)$
Whiteness	–	≥ 70
Density	[kg/m³]	2,600–2,800 (no requirements)

4. Outline of boiler flue gas desulphurization process using wet limestone method

The method consists in contacting flue gas with limestone water slurry in an absorber. When absorption slurry is being prepared and calcium carbonate is introduced into a tank, its dissociation takes place to the degree determined by its solubility

$$CaCO_3(s) \rightarrow CaCO_3(aq) \tag{1}$$

$$CaCO_3(aq) + H_2O \rightarrow Ca^{2+} + HCO_3^- + OH^- \tag{2}$$

In absorption zone of the absorber, SO2 is dissolved in water

$$SO_2(g) \rightarrow SO_2(aq) \tag{3}$$

$$SO_2(aq) + H_2O \rightarrow HSO_3^- + H^+ \tag{4}$$

$$HSO_3^- \rightarrow H^+ + SO_3^{2-} \tag{5}$$
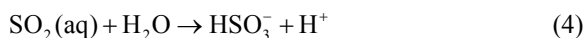
Sulphite anion joins calcium cation forming insoluble semi-aqueous calcium sulphite

$$Ca^{2+} + SO_3^{2-} + 1/2\,H_2O \rightarrow CaSO_3 \cdot 1/2\,H_2O(s) \tag{6}$$

Following the oxidation of sulphite anion into sulphate anion, the second insoluble product of flue gas desulphurization, i.e. synthetic gypsum, is generated.

$$SO_3^{2-} + 1/2\,O_2 \rightarrow SO_4^{2-} \tag{7}$$

$$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O(s) \tag{8}$$

As a result of reactions (6) and (7), calcium cations are removed from the solution, which – according to the solubility product – generates further solution of calcium carbonate.

Additional oxygenation of $CaSO_3$ causes its conversion into $CaSO_4$ which, upon precipitation, is subjected to treatment (washing and dewatering) to get the final product of synthetic gypsum ($CaSO_4 2H_2O$). Limestone dust is initially prepared as water slurry in appropriate installation. Then, it is pumped into the absorber. A special arrangement of circulation pumps, pipelines and sprayer system ensures intense spraying of flue gas in the absorption tower. The efficiency of desulphurization process is greatly dependent on the contacting intensity between flue gas and atomized limestone slurry determined by L/G parameter expressed by the ratio of volumetric stream of the sprayed slurry to volumetric stream of flue gas subjected to desulphurization in the absorber, (dm^3/m^3). The efficiency of flue gas desulphurization is also dependent on the following parameters: flue gas temperature and pressures, fractions of $CaCO_3$, MgO, aluminosilicates and other components included in the milled limestone batched into the retention tank of absorption liquid, as specified in Tab. 1, and on the sorbent reactivity for sulphur oxides subjected to removal from gas phase (IV and VI) [4]. A generic flow diagram of flue gas desulphurization installation using wet limestone method is shown in Fig. 2. The process solution shown in Fig. 2 for flue gas desulphurization enables to obtain from desulphurization such a product of synthetic gypsum whose properties are not worse than those of the natural gypsum.
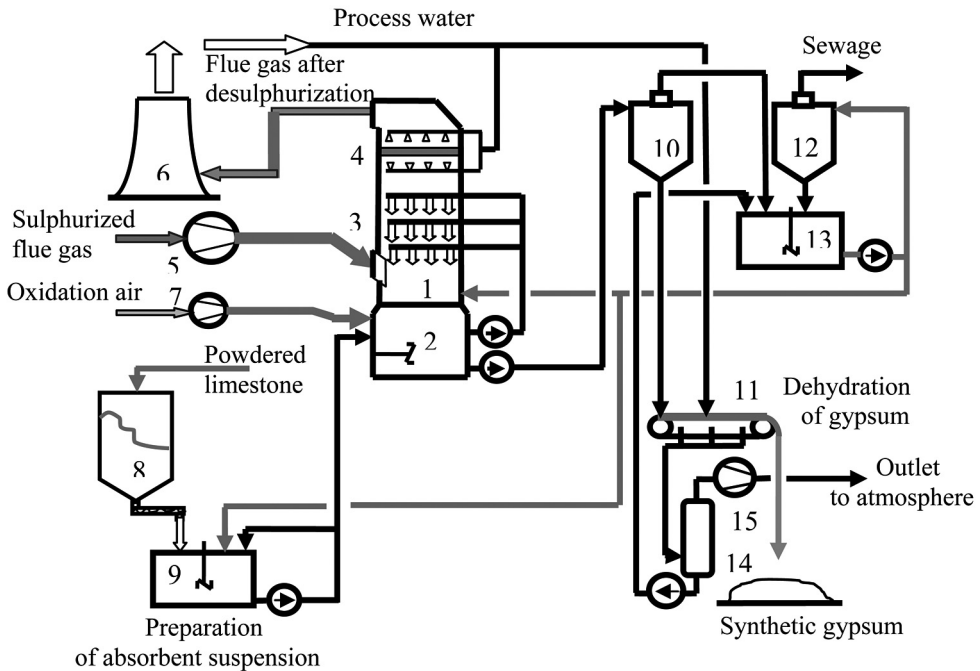
Fig. 2. Flow diagram of flue gas desulphurization using wet limestone method. 1 – cooling tower, 2 – absorption slurry tank, 3 – section of flue gas spraying in absorber, 4 – droplet separator, 5 – flue gas flow boosting fan, 6 – blower for slurry oxygenating air, 7 – silo of powdered sorbent (milled limestone), 8 – tank of fresh sorbent slurry, 9 – bank of gypsum slurry hydrocyclones, 10 – vacuum band filter, 11 – filtrate tank, 12 – bank of effluent hydrocyclones, 13 – tank of circulation water

Rys. 2. Schemat instalacji odsiarczania spalin mokrą metodą wapienną. 1 – chłodnia kominowa, 2 – zbiornik zawiesiny absorpcyjnej, 3 – sekcja zraszania spalin w absorberze, 4 – odkraplacz, 5 – wentylator wspomagający przepływ spalin, 6 – dmuchawa powietrza natleniającego zawiesinę, 7 – silos sproszkowanego sorbentu (zmielonego wapienia), 8 – zbiornik świeżej zawiesiny sorbentu, 9 – bateria hydrocyklonów zawiesiny gipsu, 10 – filtr próżniowy taśmowy, 11 – zbiornik filtratu, 12 – bateria hydrocyklonów ścieków, 13 – zbiornik wody obiegowej

Efficiency of flue gas desulphurization (FGD) in the absorber depends on many variable parameters. Figures 3 and 4 illustrate the effect of selected operating parameters of FGD (like flue gas velocity in absorber, SO_2 concentration in flue gas at absorber inlet, pH value of absorption slurry, L/G ratio) for power unit in power plant combusting brown coal. It was found that SO_2 removal efficiency decreases when flue gas velocity in absorber and SO_2 concentration before entering the absorber increase, and when the pH value and L/G ratio decrease [5].
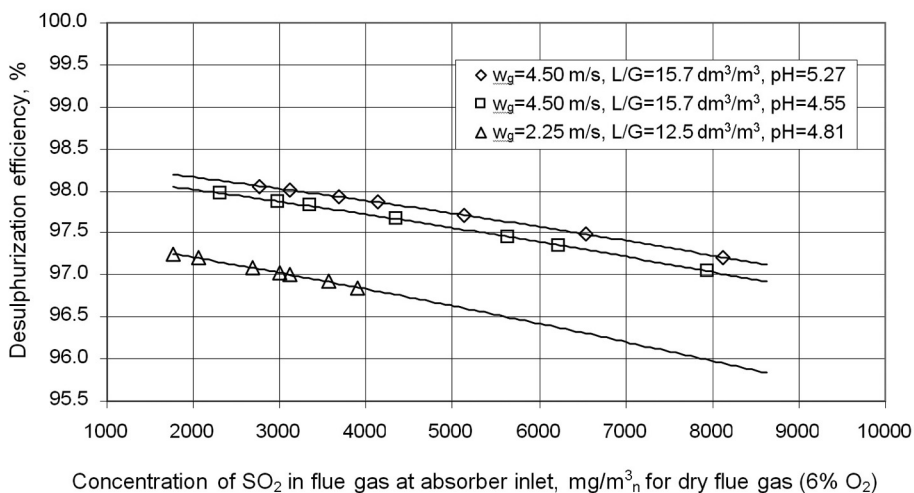
Fig. 3. Desulphurization efficiency versus SO$_2$ concentration, flue gas velocity at absorber inlet, L/G ratio and pH value of absorption slurry

Rys. 3. Zależność skuteczności odsiarczania od stężenia SO$_2$ i prędkości spalin na wlocie do absorbera oraz stosunku L/G i wartości pH zawiesiny absorpcyjnej
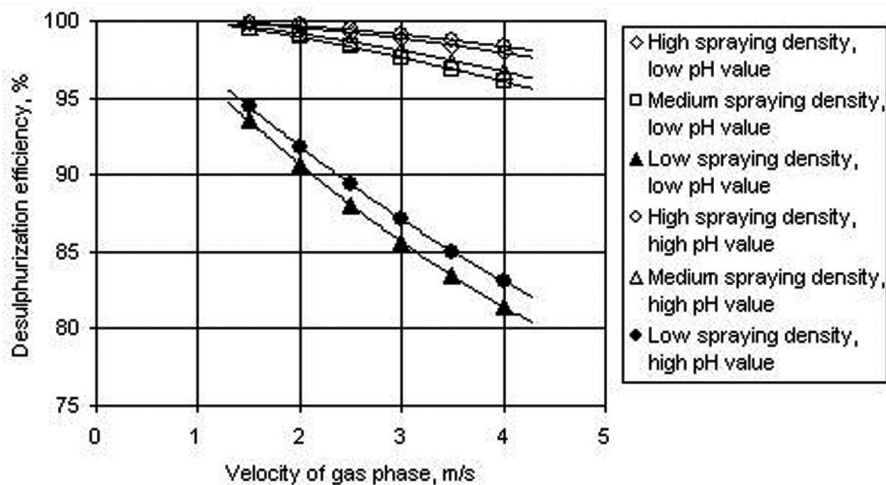

Fig. 4. Desulphurization efficiency versus flue gas velocity in absorber at high and low pH values of absorption slurry, and at low, medium and high spraying densities

Rys. 4. Zależność skuteczności odsiarczania od prędkości spalin w absorberze w warunkach dużych i małych wartości pH zawiesiny absorpcyjnej oraz małych, średnich i dużych gęstości zraszania

5. Characterization of synthetic gypsum

According to equation (8), the product of flue gas desulphurization is dihydrate, synthetic gypsum, which is fed into stores or transferred to building materials factory (e.g. fabricating gypsum plasterboards). Usually, the factory is located in the vicinity (most often just beside) a flue gas desulphurization plant and gypsum is transported via encased belt conveyors. In order to transform the product into semi-hydrate synthetic gypsum ($CaSO_4 \cdot \frac{1}{2}H_2O$), i.e. the building grade of gypsum, it needs to be dried and then roasted at about 150–160°C.

Synthetic building-grade gypsum is commonly used in the USA, Japan and Germany. Also in Poland, its volume of production rises increasingly as new flue gas desulphurization plants are launched in domestic power plants. The first flue gas desulphurization (FGD) plant using wet limestone method in Poland was constructed under licence of the Dutch Hoogovens Technical Services Energy & Environment Company in Bełchatów Power Plant on Power Unit No. 8 in September 1994 [6]. Three successive plants were commissioned for Power Units Nos. 10, 11 and 12 in 1995-1996. Successive FGD plants, for Power Units Nos. 5, 6, 7, 9 and 3, 4 were designed and fabricated by the Polish company RAFAKO S.A. in 2000–2007.

At present, Bełchatów Power Plant is the largest manufacturer of synthetic gypsum in Poland as FGDs are operated on 10 power units (each with the power of 370 MW, maximum throughput of 2,100,000 m^3_n/h of raw flow gas and gypsum mass about 50 Mg/h at humidity up to 10%). Now, the Unit No. 13 (with power of 858 MW) is under commissioning. The unit is equipped, due to very large volumetric flow of flue gas, with two plants (each with the capacity of 1,800,000 m^3_n/h of raw flue gas and gypsum production of 62.1 Mg/h at moisture content up to 10%).

Calcium sulphate dihydrate, generated in the flue gas process, is subjected to examinations for its grain composition and chemical analysis. Exemplary grain composition of synthetic gypsum fabricated in boiler flue gas desulphurization process in one of Polish power plants is shown in Fig. 3. The grain composition analysis, providing particular volumetric (mass) fractions and their cumulated distribution was done with laser particle size meter, the HELOS BR type, made by Sympatec. Determinations were also made for synthetic gypsum density and specific surface of its particles. They are: $\rho = 2.710$ g/cm^3 and $S_m = 604.2$ cm²/g, respectively.
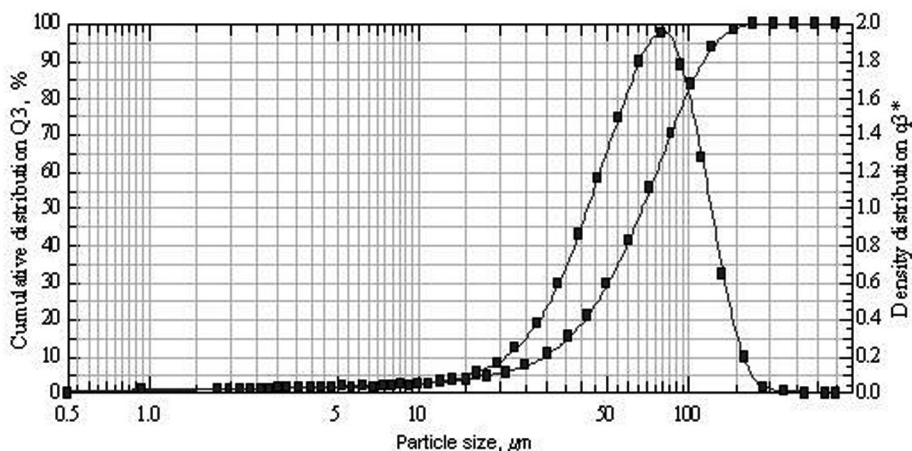
Synthetic building gypsum has similar chemical composition and properties to those of the natural gypsum, especially after hardening, however its compression strength is higher than that of the natural gypsum (by c. 35–40%) and has very short time of set. It is distinguished by its cream colour. It has diversified grain size distribution, hence it is of worse workability. The sample chemical analysis of synthetic gypsum is presented in Tab. 2.

Examinations made for the concentration of natural radioactive isotopes: potassium K-40, radium R-226 and thorium Th-232 allowed to determine the indexes according to Instruction ITB 234/95. They were as follows [7, 8]:
– $f_1 = 0.026$–0.005, which represents 2.6% of admissible value ($f_1 \leq 1,2$ [4]),
– $f_2 = 7.73$ Bq/kg, which represents 4.2% of admissible value ($f_2 \leq 240$ Bq/kg [4]).

These are levels similar to those of the natural gypsum. All comparisons and references of synthetic gypsum properties with respect to the natural one confirm the belief that this material, as concerns its effect on human health, is comparable with lime and wood.

x_{10} = 29.61 µm x_{50} = 67.48 µm x_{90} = 115.16 µm   SMD = 36.64 µm   VMD = 70.10 µm

x_{16} = 37.18 µm x_{84} = 103.02 µm x_{99} = 158.22 µm S_V = 0.16 m²/cm³ S_m = 604.20 cm²/g

Fig. 5. Grain composition of synthetic gypsum (CaSO$_4$·2HO). $x_{10}…x_{99}$ – diameters of particles whose cumulated fractions represent less than 10…99% volume of all particles, SDM – average superficial diameter of particle set, VMD – average volumetric diameter of particle set, S_v – specific surface area of particles per unit of volume, S_m – specific surface area of particles per unit of mass, $q3* – q3$(log)

Rys. 5. Skład ziarnowy gipsu syntetycznego (CaSO$_4$·2HO). $x_{10}…x_{99}$ – średnice cząstek, których skumulowane udziały stanowią mniej niż 10…99% objętości wszystkich cząstek, SDM – średnia średnica powierzchniowa zbioru cząstek, VMD – średnia średnica objętościowa zbioru cząstek, S_v – powierzchnia właściwa cząstek odniesiona do ich objętości, S_m – powierzchnia właściwa cząstek odniesiona do ich masy, $q3* – q3$(log)

New gypsum processing plants are launched in Poland following new FGD plants commissioned in power plants. The KNAUF factory was constructed beside Bełchatów and Jaworzno Power Plants, the Norgips Plant was launched beside the Opole Power Plant, the Dolina Nidy branch plant was situated next to the Patnów–Konin–Adamów Power Plant, while synthetic gypsum from the Dolna Odra Plant is collected by Lafarge – Cement Polska S.A. A similar situation is found in the case of successive power plants launching GFD plants. In this way such companies as Knauf, Norgips, Atlas (Dolina Nidy), Lafarge – Cement Polska S.A. contribute to the direct protection of natural environment of human beings.

In order to get a full-value building material from post-reaction gypsum, it should be subject to the calcination (roasting) process at 150–180°C.

The binder fabricated this way can be used to produce such building elements as:
– gypsum boards fabricated according to KNAUF, NORGIPS or other technologies suitable for general and industrial building processes,
– large-size wall gypsum boards, reinforced and non-reinforced, applicable in general and industrial building to construct partition walls,
– foam/gypsum elements acc. to SOVA-System-House technology,

– mould-less building elements with pipes used as formwork,
– gypsum/ash elements used in general and industrial building,
– inter-wall gypsum elements,
– self-levelling floors.

Chemical analysis of synthetic gypsum

Parameter	Contents [%] mass	Balance
SiO_2	2.0	
Fe_2O_3	0.0	
Al_2O_3	0.4	
Mn_3O_4	0.0	
TiO_2	0.02	
CaO	31.5	
MgO	0.22	
SO_3	44.9	
P_2O_5	0.0	
Na_2O	0.01	$CaSO_4 \cdot 2H_2O = 96.27\%$
K_2O	0.05	$CaCO_3 = 0.06\%$
Cl^-	0.005	$CaSO_3 \cdot \frac{1}{2}H_2O = 0.97\%$
F	0.05	$Ca(OH)_2 = 0.0\%$
Calcination loss at 900°C	20.0	$CaCl_2 = 0.01\%$
In total	99.1	$CaF_2 = 0.01\%$
Free CaO	0.0	Contents of neutral components
Soluble fluorides	0.005	$(SiO_2 + Al_2O_3 + Fe_2O_3)$: 2.39%
Sulphites as SO_3	0.48	
Sulphates as SO_4	53.15	
Soluble potassium as K_2O	0.002	
Carbonates as CO_2	0.03	
Soluble magnesium as MgO	0.013	
Soluble chlorides	0.005	
Whiteness	82 %	

Among building binders based on post-reaction gypsum, of interest are dry gypsum mixtures: plaster gypsum, gypsum putty, gypsum adhesives. In the cement manufacturing technology, gypsum is one of components used to control cement setting time. As such an additive, it amounts to 4–4.8% of cement mass. Such function can be served by post-reaction gypsum of appropriate quality, in an agglomerated form (briquettes, granulated products) or in a loose form. They meet the requirements of PN-EN 13279-1:2007 Standard and tightened environmental control criteria resulting from the requirements of DIN EN ISO 14001:2005 Standards.

6. Conclusions

Experience gained both in foreign and domestic power plants as well as cogeneration plants demonstrated that limestone, including over 95% of calcium carbonate and used as SO_2 sorbent in desulphurization process for boiler flue gas generated in hard and brown coal combustion, is distinguished by its very good sorption properties.

When the process and operating parameters are properly selected, it is possible to run flue gas desulphurization using wet limestone method at efficiency of 95% or even over 99% while maintaining the sorbent excess coefficient within 1.02–1.05 with respect to SO_2 content in flue gas.

The final product of flue gas desulphurization is calcium sulphate dihydrate called synthetic gypsum including over 95% of $CaSO_4·2H_2O$ and up to 10% of moisture whereas all other parameters are within the admissible limits specified in PN-EN 13279-1:2007 Standards and comply with the requirements of DIN EN ISO 14001:2005 Standards.

The way of both limestone use in the flue gas desulphurization by wet limestone method and the final product fabrication meets all the conditions necessary to recognize the sorbent-to-synthetic gypsum transformation by FGD technology as classic recycling.

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