

UTILIZATION OF FLUE GAS DESULPHURIZATION BY-PRODUCTS IN THE CELLULAR CONCRETE TECHNOLOGY

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ABSTRACT

In the fly gas desulfurization processes by use of other methods than the wet lime one, or during the fluidized bed combustion, the waste materials, being the mixture of fly ash, desulfurization products and residual sorbent are usually produced. Their complex and very often variable chemical and mineralogical composition is a factor substantially limiting the possibility of their reuse.

In this work the chemical and mineral composition of wastes produced in different desulfurization processes has been determined. These wastes were used as a natural gypsum replacement in the so-called PGS cellular concrete technology („foamed-gaseous-silicate concrete”). The growth of fresh mixture, phase composition of fresh and hardened concrete, morphology of hydration products and practical properties of hardened cellular concrete were examined. As it results from the studies, the waste material from desulfurization process can be used as a component in cellular concrete technology. The fly ash can play a role of fine-grained aggregate or cementitious material.

1. INTRODUCTION

The reduction of sulfur and nitrogen oxides emission to atmosphere is nowadays one of the most important tasks in the natural environment protection. The desulfurization and denitrification programs can be realised effectively when the efforts in the field of coal desulfurization, flue gas desulfurization and denitrification and waste disposal are co-ordinated.

Among the over 100 methods of flue gas desulfurization invented until now, only some of them have been put into practice. The wet lime method should be pointed out as the first one. In some countries, where the desulfurization operation has been advanced early (USA, Japan, Germany), more than 80% of desulfurization installations work following this wet lime method, in which the de-dusted gases are subjected to the purification. The pure gypsum dihydrate, produced as a desulfurization product, can subsequently substitute the natural gypsum raw material in building materials production and in other technologies.

When the desulfurization waste material is a multicomponent mixture of fly ash, desulfurization products, unreacted sorbent and other compounds formed on fuel combustion, the other technologies should be taken into account. The authors are of the opinion that the Polish cellular concrete technologies PGS or UNIPOL (fly ash or combined variant) can be useful for this purpose.

The experiments aimed with the determination of different flue gas desulfurization by-products usability in cellular concrete technology by PGS method. The calcium sulfates and sulfites from waste material controlled the growth and setting of concrete mixture, and consequently the strength development of cellular concrete. The gypsum component, which is commonly used in the first step of cellular concrete technology, acts as a calcium aluminate and aluminoferrite hydration retarder. It reacts quickly with these phases, originating from fly ashes and cement, as well as with the hydrated calcium aluminates produced in reaction between Al powder and Ca^{2+} ions from the solution. On the surface of Al powder particles the ettringite and hydrated calcium monosulfate are thus formed and hinder the hydrogen release. The AFt and AFm phases have no special influence on the properties of hardened concrete, because they fill the pores on growth and early maturing.

The proper growth of concrete mixture is disturbed at low gypsum component content. The quick setting is thus observed and the mixture does not attain the right structure [1].

At the presence of calcium sulfites $\text{C}_3\text{A}\cdot\text{CaSO}_3\cdot 12\text{H}_2\text{O}$ is formed instead of ettringite [2]. This compound oxidates to ettringite [2,3].

2. EXPERIMENTAL

2.1. Materials

2.1.1. Fly ash „Skawina”

The fly ash was produced from the black coal in the „Skawina” power station. It complies with the standard requirements for the raw materials used in cellular concrete production. The chemical composition of fly ash is given in Table 1.

- | | |
|--------------------|----------------------------------|
| • specific gravity | 2.12 g/cm ³ |
| • specific surface | 3050 cm ² /g (Blaine) |
| • water demand | 27% |

2.1.2. Ground burnt lime „Tarnów Opolski”.

The ground burnt lime complying with the standard requirements for the raw materials used in cellular concrete production was used. The properties of lime are as follows:

- active CaO + MgO content 87.1%
- time of slaking 28 min
- temperature of slaking 68°C
- total CaO content 93.5%
- total MgO content 3.4%
- loss on ignition 3.0%

2.1.3. Flue gas desulfurization by-products.

The following FGD by-products were used:

- from wet bialkaline method („Chrzanów” thermal power station)
- from semi-dry „dry scrubbing” process („Sosnowiec” thermal power station)
- from fluidized bed combustion with desulfurization, both pressure installation (PFBC Canada) and atmospheric air circulation installation (FBC Canada).

The natural Polish gypsum raw material was also used as reference.

In Table 2 the chemical composition of materials is shown (including free CaO).

The chemical composition data for particular by-products show the significant differences between the sulfate components and free CaO contents. One should also notice the differences in sulfite contents, determined as SO₂.

The phase composition of FGD by-products was studied by XRD and DTA-TG methods. The results are shown in Table 3. In some cases the products of desulfurization reaction was not identified because of poor crystalline form or low content. Therefore the presence of particular phases was deduced rather from chemical analysis data and DTA-TG curves (they are marked by „*” in Table 3). The sulfate and sulfite contents were calculated from the chemical composition. The results of this evaluation are as follows:

- 35.9% CaSO₄·2H₂O and 15.1% CaSO₃·0.5H₂O for bialkaline process,
- 15.5% CaSO₄·2H₂O and 14.1% CaSO₃·0.5H₂O for dry scrubbing process,
- 26.8% CaSO₄ and 0.8% CaSO₃ for pressure FBC,
- 30.1% CaSO₄ and 0.9% CaSO₃ for FBC,
- 24.0% CaSO₄ for dust from FBC installation.

2.2. Examination of pastes prepared with flue gas desulfurization products.

The FGD by-products were used to produce the cementitious materials used in cellular concrete technology by PGS method. The composition of particular binders mixtures is given in Table 4. The calculations based on assumed SO₃ content, the same as in reference batch with natural gypsum component. The sulfites were calculated as equivalent to sulfates. The dry components were ground to the Blaine specific surface of ca. 4100 cm²/g.

The samples were mixed with water at water to solid ratio 0.35 and after preliminary curing at 65°C for 1 hour autoclaved at 190°C/12 atm for 12 hours cycle. The autoclaved samples were examined by XRD and SEM. The chemical composition of these samples was very similar and the two main mineral components - hydration products were detected by XRD: tobermorite Ca₅[Si₆O₁₈H₂]-4H₂O and hydrogarnet Ca₃Al₂[SiO₄](OH)₈. Some amount of calcite and β-quartz, being the unreacted residue, is also visible. The XRD patterns exhibit

some differences of peak intensities which can reflect the different contents and degree of crystallinity for particular phases. This was confirmed by SEM observations. The samples, despite of the similarity of phase composition, reveal the presence of different tobermorite and hydrogranet forms. The degree of crystallinity may be affected by the presence of sulfites, which promote the poorly crystallized, defected structures of hydration products. One can conclude that the microstructure of autoclaved pastes prepared with desulfurization by-products depends on the composition of these materials. This fact may be of significant importance in concrete technology. The average microstructures of autoclaved pastes are shown in Fot. 1-6.

2.3. Evaluation of concrete mixture growth in the presence of desulfurization products.

2.3.1. Examination of hydrogen release.

This experiment was carried out basing on the test of aluminium powder activity. The effect of different desulfurization by-products on the rate of hydrogen release the fresh concrete mixture was measured and the results are given in Table 5 and 6.

As it can be seen in Table 5 and 6 the hydrogen release depends on the composition of concrete mixture, particularly on the content of sulfites. At high sulfite content, as in the sample with desulfurization by-product II from semi-dry process, the reaction of Al powder with calcium hydroxide is strongly hindered. The experiment has been carried out for a long time in this case, with and without agitation of mixture. This is of interest that the hydrogen release is not stopped and agitation improves it significantly.

2.3.2. Examination of fresh concrete mixtures.

The concrete mixtures were produced following the proportions taken from PREVAR (concrete prefabrication plant in Skawina near Kraków in Poland):

- dry components for 1 m³ of concrete - 620 kg, including 312 kg of cementitious material and 308 kg of fly ash „Skawina”,
- water - 310 l (w/s = 0.5),
- Al powder - 380 g,
- surfactant as 38% solution of Sulfapol - 620 g.

The procedure of concrete mix production was as follows:

Firstly the surfactant was poured to the water and, after agitation, the Al powder. Subsequently, the other components (cementitious material and fly ash) were added to this suspension and homogenized (3 min and 15 min in the case of the batch with by-product II, because of retarded hydrogen release). The mixture was poured into the moulds (ϕ 80 mm, h=80 mm). The concrete mixtures were cured at 65°C for 1 hour and subsequently autoclaved. The process was not disturbed at all.

The visual examination of samples gave positive results (only the samples with SII showed slow growth). The concretes were enough strong to remove the spews and to keep cutting.

The spews were examined by XRD, after rinsing with acetone. The similar phase composition was found with such hydrates as calcium hydroxide Ca(OH)₂, ettringite 3CaO·Al₂O₃·3CaSO₄·32H₂O, in some cases traces of calcium carboaluminate hydrate 3CaO·Al₂O₃·CaCO₃·12H₂O and hydrated calcium aluminate C₄AH₁₃.

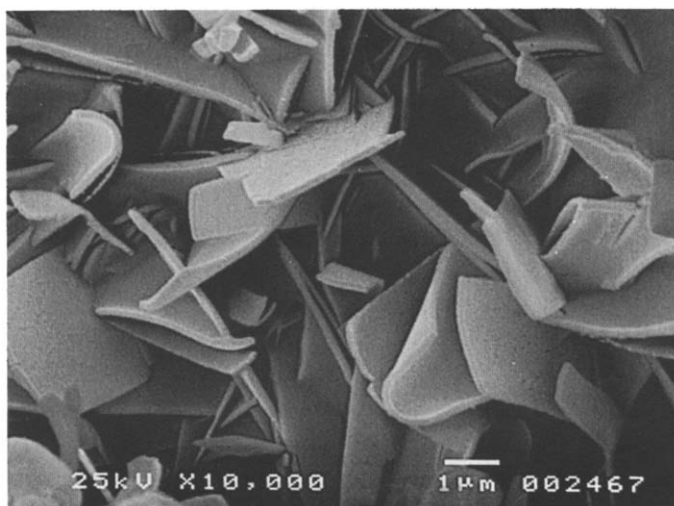
The cellular concrete samples were autoclaved in PREVAR and the elements thus produced did not exhibit any destructive effects. Because of small amount of materials in this

tests, the full examination of concretes was not possible. However, one could find a higher apparent density (5-20%) than for control sample as well as similar compressive strength and capillary suction. Simultaneously, in the opinion of authors, the concrete mixture design procedure was in this case too simplified. For industrial implementation the concrete mixture composition should be further optimized. In Table 7 the results of standard tests, according to Polish standard PN-89/B-06258, for the cellular concrete with by-product „I” from bialkaline process are shown.

3. CONCLUSIONS.

- The waste materials from different desulfurization installations show the presence of different products formed on desulfurization, being the compounds of SO_2 and SO_3 . Depending on the process these products are: gypsum dihydrate, gypsum hemihydrate or anhydrite with more or less calcium sulfite or calcium sulfite hemihydrate.
- At high amount of sulfites in waste materials used to produce the binder (even more than 50% S in sulfite) the retardation of H_2 release takes place.
- The desulfurization products affect the microstructure of autoclaved pastes and concrete mixtures. The degree of crystallinity and crystal size is strongly influenced.
- The cellular concrete samples produced with different desulfurization wastes exhibit similar or slightly less advantageous physical properties than the reference sample. This, in the opinion of authors, may be altered by better optimization.

Fot.1. Autoclaved paste prepared from reference sample S0 with well developed plate-like tobermorite crystals.



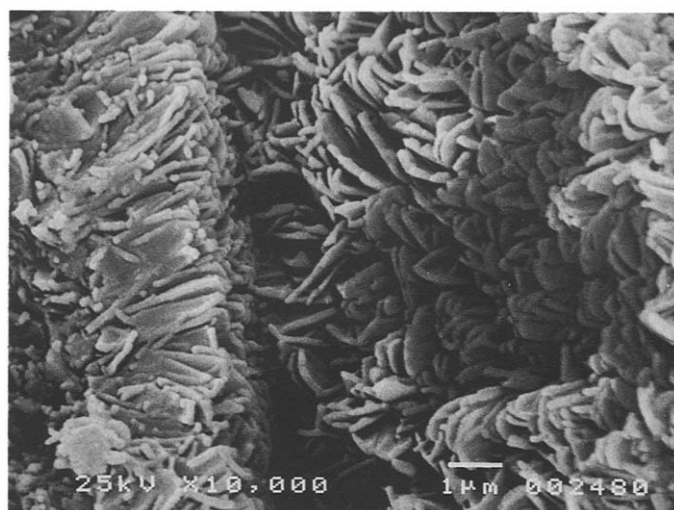


Table 1. Chemical composition of fly ash.

L.O.I. [%]	SiO ₂ [%]	Fe ₂ O ₃ [%]	Al ₂ O ₃ [%]	CaO [%]	MgO [%]	SO ₃ [%]	Na ₂ O [%]	K ₂ O [%]
1,23	53,78	8,46	26,66	6,42	1,57	0,52	1,72	3,04

Table 2. Chemical composition of FGD by-products.

Sample Number	Component in weight %								
	L.O.I.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO _c	MgO	SO ₃	SO ₂	CaO _w
I	26,04	5,94	2,86	1,05	41,94	0,95	16,72	7,52	2,01
II	21,77	8,43	7,54	1,86	40,05	2,10	8,54	7,00	7,39
III	14,24	11,16	5,51	8,42	43,54	0,34	15,75	0,88	17,32
IV	5,08	19,87	5,75	4,28	44,23	0,59	17,71	0,94	15,34
V	24,21	12,00	6,00	11,96	30,66	0,42	14,11	-	9,93

I - material from bialkaline process („Chrzanów”)

II - material from dry scrubbing process („Sosnowiec”)

III - material from pressure FBC installation („Canada”)

IV - material from FBC installation with atmospheric air circulation („Canada”)

V - material from dedusting of FBC installation gases

Table 3. Phase composition of FGD by-products.

Phase	Flue gas desulfurization by-product (as in Table 2)				
	I	II	III	IV	V
CaSO ₄ ·2H ₂ O,	+				
CaSO ₄ ,			+	+	+
CaSO ₄ ·0.5H ₂ O		+			
CaSO ₃ ·0.5H ₂ O,	+	+			
CaSO ₃			+	+	
CaCO ₃ ,	+	+	+	+	+
Ca(OH) ₂	+	+	+	+	+
CaO,			+	+	
βSiO ₂	+	+	+	+	+
Fe ₂ O ₃		+	+		+
3Al ₂ O ₃ ·2SiO ₂ (mullite),		+			
3CaO·Al ₂ O ₃ ·3CaSO ₄ ·32H ₂ O	+				
CaSiO ₃ ·CaCO ₃ ·CaSO ₄ ·15H ₂ O	+				
unburned carbon		+			

Table 4. The compositions of binder mixtures.

Cementitious material components	Mixture number* [% by weight]					
	SI	SII	SIII	SIV	SV	SO **
FGD by-product	14,1	19,4	19,9	17,7	23,7	-
ground lime	37,7	36,6	34,6	35,3	35,6	38,0
fly ash	48,2	44,0	45,5	47,0	40,7	54,0
natural gypsum	-	-	-	-	-	8,0

* - S(I-V) - binder with FGD product as in Table 2.

** - S0 - reference binder with natural gypsum

Table 5. The effect of binders on the rate of hydrogen release.

Time [min]	Volume of H ₂ [cm ³] at t=20°C (composition of binders as in Table 4)				
	SI	SIII	SIV	SV	S0
2	0,5	0,5	0	0	0
8	9	10	28	8	6
16	44	46	63	32	61
20	58	-	-	-	-

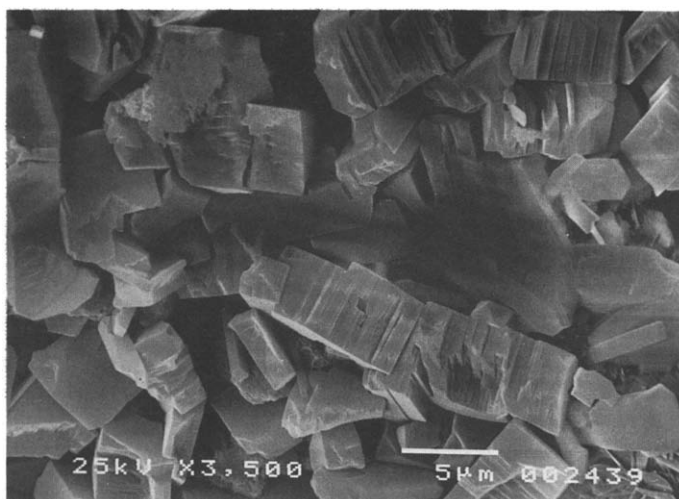
Table 6. The effect of binder SII on the rate of hydrogen release.

Time [min]	Volume of H ₂ [cm ³] at t=20°C	
	Test following the procedure as in Table 4	Test during continuous agitation of mixture
2	0	0
8	0	0
16	1	3
20	4	7
40	35	46
56	46	66

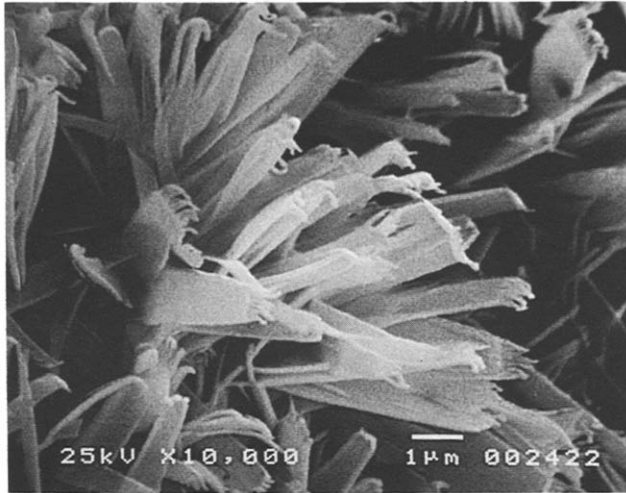
Table 7. The results of standard tests for the cellular concrete with by-product I.

Test property	Result
Volume density at dry state	av. 646 kg/m ³
Compressive strength	av. 4.30 MPa
Freeze and thaw resistance	no fissures, scalls, cracks, weight loss; compressive strength decrease of 14.3%
Capillary suction	av. 4.7 cm
Shrinkage	0.6 mm/m.
Heat conductivity coefficient at dry state - Bock's Method	0.146 W/m·K

Fot.4. Autoclaved paste prepared from sample SIII. The well developed hydrogranets are visible.



Fot.5. Autoclaved paste prepared from sample SIV with perfect tobermorite twinned forms.



Fot.6. Autoclaved paste prepared from sample SV with tobermorite crystals intergrowths.

