Basic Properties of Flue-Gas Desulfurization Gypsum

***Ferenc Kovacs and Jozsef Molnar*[1]**

Základné vlastnosti sadrovca pre odsírenie spalín

Several hundred thousand of FGD gypsum is produced annually at the Matra Power Plant (Hungary) as a byproduct of generating electricity and protecting the environment. Chemical and mechanical characteristics of this material were studied of the Department of Mining and Geotechnical Engineering, University of Miskolc (Hungary). The material in question was found dead gypsum which can be calcined easily to obtain a relatively high-strength (15-25 MPa) and clean binding material. Furthermore, grain composites were made of it by adding fly ash, which the power plant can provide the expected producers with, thus decreasing the energy consumption of calcining and utilizing a small part of coal combustion wastes.

Introduction

More than 1 million metric tons of ash and some hundred thousand flue-gas desulfurization gypsum are produced annually as byproduct materials in the lignite-fired Matra Power Plant in Hungary, obtaining fuel from its two opencast mines. Handling, disposal and utilization of such a great amount of bulk material and of the industrial wastewater created during the technological process are obviously important problems from technical, economic and environmental points of view as well.

A long-term research is being performed at the Department of Mining and Geotechnical Engineering, University of Miskolc (Hungary) to determine the main characteristics of the different coal combustion products from the power plant (Kovacs et al., 2000; Molnar and Dovrtel, 2000). Technical details, characterizing the ash have already been measured and evaluated. Presently, our attention is focused on the byproduct gypsum.

As the material can be considered as a new quite material in our country, comprehensive research is conducted to find its chemical, physical and mechanical properties. Although the research is in progress during a long term, numerous advantageous features of the gypsum, e.g. its 15-25 MPa compressive strength, etc., have already been determined concerning even its utilization. Furthermore, this relatively high strength is not decreased significantly by adding a certain amount of fly ash to gypsum, thus producing a kind of construction composite material for in-house applications using only industrial waste components. Mechanical properties such as the density, hardness and strength of the solidified material can be adjusted easily to the required value in wide ranges.

The flue-gas desulfurizing process

The new wet flue-gas desulfurizing (FGD) equipment (Hicks, 2000; Ludanyi, 2000) was established in the cooling towers of the power plant and was put into operation at the end of 2000. The reagent suspension used in the process is water containing approximately 20% fine grained limestone. It is sprayed from sprinklers mounted at the top of the equipment into the upward flue-gas stream. The vast amount of its sulfur-dioxide content is absorbed by the droplets transforming calcium-carbonate into sulfate, sulfite and sulfide.compounds. The cleaned gas is led into air at the top of the towers. The sludge is collected on and removed from the bottom of the reactor chamber. Its water content is decreased to an approximately 20% moisture content during conveying it to its disposal area where it is dumped separately from the ash, thus keeping the sludge clean.

Although the FGD equipment was originally established for environmental purposes, it was shown even by the results of the first calculations, that the formation of a great amount of synthetic gypsum can be expected during its operation. Consequently, one of the first questions was either to dispose the whole quantity as the industrial waste or to use it as a binding material, because it is shown by different statistical summaries (U.S.G.S Mineral industry surveys, 1999) that a significant quantity of byproduct gypsum is being utilized. If utilization can be profitable, what are the basic characteristics of the byproduct in question? As the FGD equipment was the first one in our country, there were no appropriate domestic experiences with it.

The raw FGD gypsum

The raw FGD gypsum is extremely fine grained material with a low moisture content. It is not surprising because the limestone powder itself is fine by grained as well to provide the necessarily high specific area for the

[1] *Ferenc Kovacs, Jozsef Molnar:* Department of Mining and Geotechnical Engineering, University of Miskolc (Hungary)
(Recenzované a revidovaná verzia dodaná 14.7.2003)

heterogeneous desulfurizing reaction. The powder looks white with a slight yellow character, containing some grey and black grains of bigger size, which can be removed with a 0,15-0,2 mm sieve if necessary.

Neither the wet nor the dried raw gypsum could be solidified after mixing with the potable water. But the vast majority of the wet powder agglomerates during some weeks when kept in closed plastic bags. The strength of the agglomerated blocks is obviously low.

Consequently, a processing is required to make the raw FGD gypsum saleable construction binding agent. This processing method is obviously calcining.

Composition of the calcined FGD gypsum

It was supposed that the raw FGD gypsum consists of primarily gypsum ($CaSO_4 \cdot 2H_2O$), bassanite ($CaSO_4 \cdot 1/2H_2O$), anhydrite ($CaSO_4$), calcite ($CaCO_3$) and some fly ash and carbon grains. Temperatures of the gypsum-bassanite and bassanite-anhydrite conversions for the material were determined by the differential thermoanalysis (DTA) measurements. These were found 120°C and 200°C.

Numerous samples were made to select the appropriate heating temperature in the 80-220°C range. Their components of crystallized form were determined by the X-Ray diffraction measurements. None of the samples contained calcite showing a perfect conversion of the limestone grains in the FGD reactor. Only gypsum was found in the solidified and the raw material, and bassanite in the samples made by heating them between 105°C and 180°C. The probes heated at the temperature of 220°C consisted of the bassanite and anhydrite mixture. One of the probes was kept at 80°C for 3 days resulting a perfect gypsum-bassanite conversion. Any other crystallized component was shown by the X-Ray measurements.

According to the results any temperature between 105°C and 180°C was found to e appropriate to transform the raw material into a bindable agent.

Standardized characteristics of the FGD gypsum

Three basic properties, such as the grain size, time of setting and the compressive strength of the gypsum are subjected to regulations in the Hungarian Standards if it is meant to be less utilized as a construction binding material.

The FGD gypsum in question proved to be fine-grained as the grain size of than 0.12-0.28% exceeds 0.2 mm. The standardized upper limit is 2% for this category. The average grain size was measured to be 0.042-0.043 mm.

The initial time of setting measured with the Vicat-apparatus was found 16-19 min, the final time 23-37 min. It can be considered a medium and long, which is quite favorable for the prefabricating wallboard elements or for many other industrial application.

The compressive strength of the material was determined by compressing ∅40 mm diameter and 60 mm high cylindrical probes, which were made of mixture of water and gypsum, containing 45% water per unit of

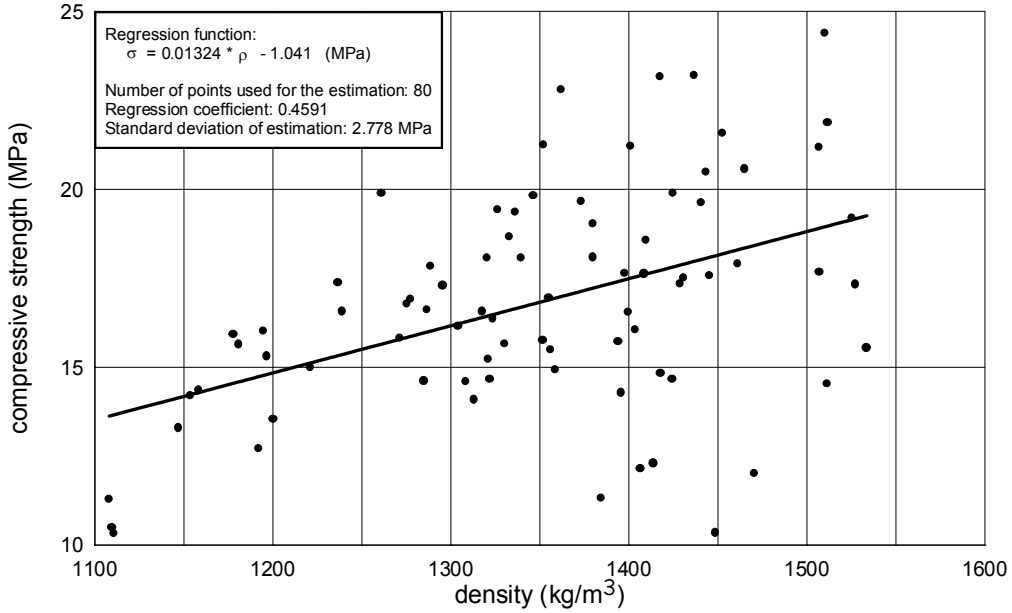

Fig.1. Compressive strength as a function of density of 80 probes, made of the FGD gypsum tfom the first calcining trials.

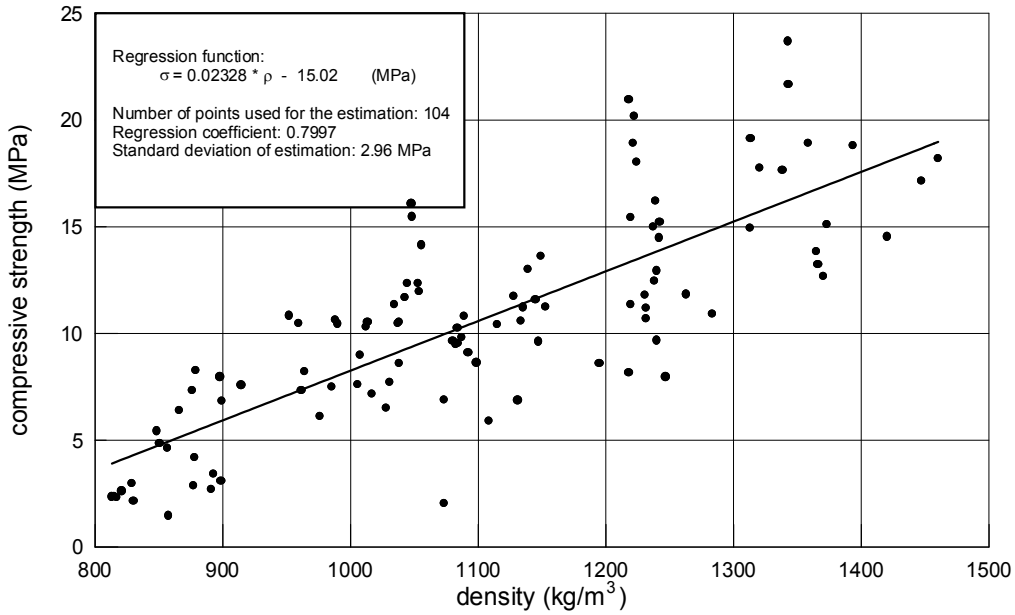

Fig.2. Compressive strength as a function of density of 104 composite probes, made of the mixture of FGD gypsum and fly ash captured by the electrofilter.

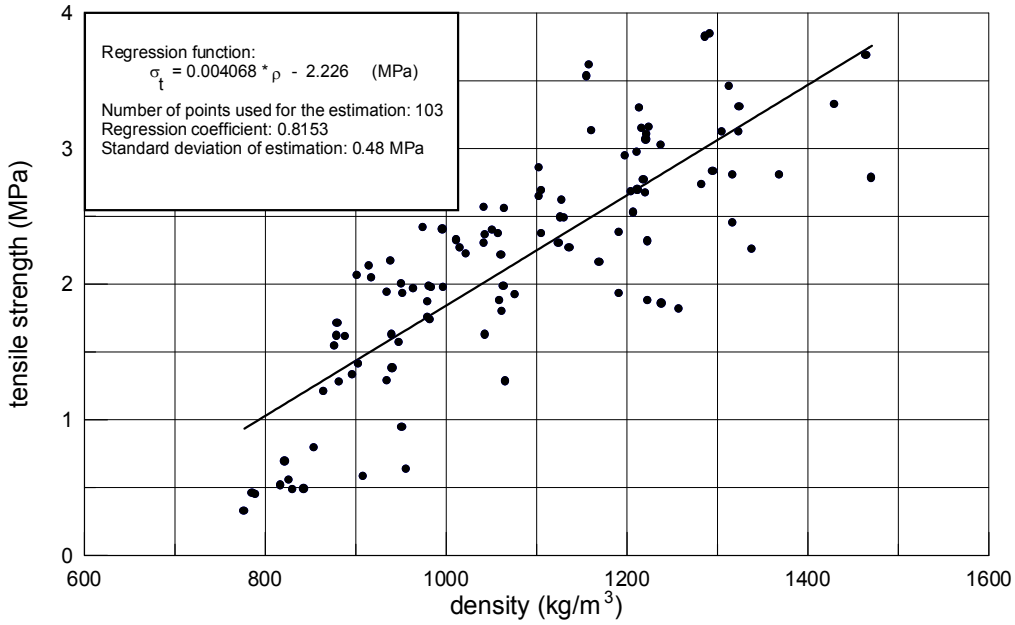

Fig.3. Tensile strength as a function of density of 103 composite probes, made of the mixture of FGD gypsum and fly ash captured by the electrofilter.

mass of the solid component. The tensile strength was measured by the brazil-test of ∅40 mm diameter and 20 mm high cylindrical probes made of the same material.

The first measurements were performed using the gypsum of the first calcining trials. It was shown even by these initial tests that a significant compressive strength (15-25 MPa) can be obtained as shown on Figure 1 as a function of density of 80 probes. The usual strength of gypsum available for the commercial use ranges between 5 MPa and 10 MPa. A poor correlation was found due to the high standard deviation of the calcining temperature and the vheating time. The tensile strength was lower 5-10 times than the compressive one as it was expected.

Further tests were performed in order to compare the strength of pure FGD gypsum with the gypsum-fly ash composite ones. Water is contained as well in the basic mixture of these composites beside the solid constituents, influencing their character.

The compressive and tensile strength are shown in Figures 2 and 3 as a function of the density (Kis, 2002). Despite a more complicated character of the composites, correlation was found to be obviously better than shown in Figure 1 for the pure FGD gypsum due to the strict calcining method. Probes made of maximum 70% gypsum and accordingly 30% water could be produced with our laboratory equipment. A similar strength was measured for composites made of 50% gypsum, 15% fly ash as filler and accordingly 35% water. A 20% decrease in the gypsum content can be the significant in cutting cost if grey colour of the products can be allowed instead of white.

Concluding remarks

The flue-gas desulfurizing blocks were equipped in the cooler towers of the Matra Power Plant to fulfill environmental regulations. Despite their high sulfur-dioxide absorbing efficiency, the dead byproduct gypsum is practically free of components (e.g. calcite, anhydrate, etc.) which cannot be made bindable agent by the normal calcining method. This is favorable in producing saleable product from this industrial waste.

Beside the advantages of reducing sulfur-dioxide emission, a possibility of cutting costs for the environmental protection is given as well. The FGD gypsum as a byproduct proved to be an excellent basic material producing a relatively high-strength gypsum primarily for the recent and future construction applications. According to the research, which is being performed at the Department of Mining and Geotechnical Engineering, the same compressive strength can be obtained if prefabricated products are made of composites instead of pure gypsum. By adding 15% fly ash and 5% extra water to the basic mixture the decrease in gypsum content is 20%. Consequently further cuts of costs can be achieved if grey colored products are allowed instead of white.

References

DEPARTMENT OF MINING AND GEOTECHNICAL ENGINEERING, UNIVERSITY OF MISKOLC (HUNGARY): Basic Parameters of Flue-Gas Desulfurization Gypsum from the Matra Power Plant (in Hungarian lagnuage). Report, 2001.

HICKS, T. G.: (editor) Power Plant Evaluation and Design Reference Guide. The McGraw-Hill Engineering and Reference Guide Series. *McGraw-Hill Book Company*, 2000

LUDANYI, GY: Construction of Flue-Gas Desulfurizing Equipment at the Matra Power Plant (in Hungarian language). BKL Banyaszat, Vol.134, 2000, pp.468-473.

KIS-PAL, L.: (candidate for diploma in materials engineering) Strength of composites made of FGD gypsum and fly ash (in Hungarian language). Thesis (instructor: MOLNAR, J.), University of Miskolc, (Hungary), 2002.

KOVÁCS, F. and MANG, B.: Solid and fly ash materials of brown coal power plants, their characteristics and utalisation. *Acta Montanistica Slovaca.* Vol. 7, 2002, 3, pp.156-160.

KOVACS, F., MOLNAR, J., VALASKA, J. and GAL, I.: Chemical and Mechanical Characteristics of Hungarian Lignite Combustion Products. 18th World Mining Congress, Coal Techniques Session, October 10, 2000, Las Vegas (U.S.A.).

MOLNAR, J. and DOVRTEL, G.: Handling and Transportation of Lignite Ash in a Hungarian Power Station. Hydromechanization 11, International Innovation Seminar 2000, Magdeburg (Germany).

MOLNAR, J. and DOVRTEL, G.: Basic Parameters of Gypsum from Flue-Gas Desulfurization Equipment (in Hungarian language). BKL Banyaszat, Vol.134, pp. 474-479.

MINERAL INDUSTRY SURVEYS, U.S.G.S.: Coal Combustion Products, 1999 Annual Review (prepared by Rustu S. Kalyoncu). U.S. Department of the Interior.

MINERAL INDUSTRY SURVEYS, U.S.G.S.: Gypsum, 1999 Annual Review (prepared by Donald W. Olson). U.S. Department of the Interior.