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LITOTAMNIJSKI KREČNJAK LEŽIŠTA „DOBRILOVIĆI“ U ODSUMPORAVANJU DIMNIH GASOVA MOKRIM POSTUPKOM[**]

Izvod

U ovom radu su dati rezultati ispitivanja litotamnijskog krečnjaka iz ležišta „Dobrilovići“, za upotrebu u odsumporavanju dimnih gasova mokrim postupkom. Prema uslovima tehnološkog postupka, ODG krečnjak treba da ispuni određene kriterijume da bi mogao da se koristi u tu svrhu. Imajući u vidu te kriterijume, u ovom radu su ispitivani hemijski sastav, nasipna masa, granulometrijski sastav i Bondov radni indeks. Rezultati ovih ispitivanja su pokazali da krečnjak ležišta "Dobrilovići" prema svojim fizičko-hemijskim karakteristikama potpuno odgovara za upotrebu u procesu odsumporavanja dimnih gasova u termoelektranama, kao i za dobijanje praškastog (rasutog) gipsa.

Ključne reči: *odsumporavanje dimnih gasova mokrim postupkom, lithotamnijski krečnjak, fizičko-hemijske karakteristike, praškasti (rasuti) gips*

1. UVOD

U okviru Nacionalnog programa zaštite životne sredine Republike Srbije, koji je donet u skladu sa Zakonom o zaštiti životne sredine, planirane su mere za održivi razvoj i upravljanje životnom sredinom u Republici Srbiji za narednih 10 godina. Jedan od prioritetnih ciljeva zaštite životne sredine u sektoru energetike, u periodu 2005.-2014. godine, je smanjenje emisije sumpornih oksida iz velikih postrojenja za sagorevanje kao što je TE Kostolac B i Termoelektrane Nikola Tesla A i B i novi termo kapacitet na kolubarski lignit približne snage 700 MW[1].

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U cilju zaštite vazduha na blokovima ovih termoelektrana ugradeni su samo uredaji za prečišcavanje dimnih gasova od čestica, elektrofilteri, ali nisu preduzete mere za smanjenje emisija sumpornih oksida, tako da njihove koncentracije u dimnom gasu višestruko premašuju dozvoljene vrednosti, kako domaće, tako i regulative Evropske zajednice. [2]

Sam sistem odsumporavanja se sastoji od postrojenja za prečišćavanje dimnih gasova vlažnim postupkom, takozvano pranje gasova, sa suspenzijom krečnjaka, a što bi se obavljalo u delu postrojenja nazvanim abzorberom. Pranje gasova se vrši tako što se struja dimnog gasa uvodi u abzorber u kojem se u vidu kiše ili kapljica uvodi suspenzija krečnjaka i u tom procesu sumpordioksid reaguje sa kalcijumom u krečnjaku i iz toga nastaje gips u vidu suspenzije, a koja se kasnije suši i odvozi u skladište gipsa, ili na mesto gde će se deponovati i spremiti za kasniju upotrebu. Precišceni gasovi se vode u dimnjak i izbacuju u atmosferu. Jasno je da je za proces odsumporavnja potrebna velika količina krečnjaka koja se dovozi iz rudnika krečnjaka. [3] Krečnjak za odsumporavanje se dobija eksplaoatacijom u rudnicima i preradom u kamenolomima rovnog materijala na zadate uslove kvaliteta. Zatim se kao takav transportuje do skladišta krečnjaka pri postrojenju za odsumporavanje.

Suspenzija gipsa koja nastaje kao nusprodukt procesa odsumporavanja primenom vlažnog krečnjačkog postupka je potencijalna sirovina za dobijanje gipsa. Pri tom kvalitet gipsa zavisi od više faktora, a prvenstveno od kvaliteta ulaznih sirovina (krečnjaka i vode). Da bi se obezbedio zahtevani kvalitet gipsa biće potrebno rekonsturisati i elektrofilter da bi se smanjila koncentracija čestica u dimnom gasu.

U ovom radu su dati rezultati ispitivanja litotamnijskog krečnjaka iz ležišta „Dobrilovići“, za upotrebu u odsumporavanju dimnih gasova mokrim postupkom. Ispitivanja su obuhvatala određivanje vlage, hemijskog sastava, nasipne mase, granulometrijskog sastava i Bondovog radnog indeksa.

2. EKSPERIMENT

2.1. Materijal i uređaji

Polazni uzorak je predstavljao krečnjak litotamnijakog porekla, ležišta Dobrilović kod Loznice. Njegov granulometrijski sastav je prikazan u tabeli 1.

Tabela 1. *Granulometrijski sastav ulaznog krečnjaka*

Klasa krupnoće, mm	M, %
-200 + 100	34,00
-100 + 50	34,00
- 50 + 30	12,00
- 30 + 0	20,00
∑	100,00

Oprema koja je korišćena u eksperimentima: laboratorijska čeljusna drobilica Wedag, 5”x6”; laboratorijska valjkasta drobilica „Denver“; laboratorijsko vibaciono sito „Kefama“; laboratorijska sušara „Heraus“; menzura zapremine 1l; atomski adsorpcioni spektrofotometar „Perkin Elmer 703“.

3. REZULTATI I DISKUSIJA

Polazni uzorak krečnjaka je usitnjen dvostepeno, prvo na čeljusnoj drobilici (Wedag, 5”x6”) i kasnije na valjkastoj drobilici (Denver), sa prosejavanjem na laboratorijskom vibacionom situ (Kefama), do krupnoće 100% -20 mm. Naime, jedan od zahteva za kvalitetom krečnjaka koji se koristi za odsumporavanje dimnih gasova mokrim postupkom jeste da ima krupnoću -19,05+0 mm.

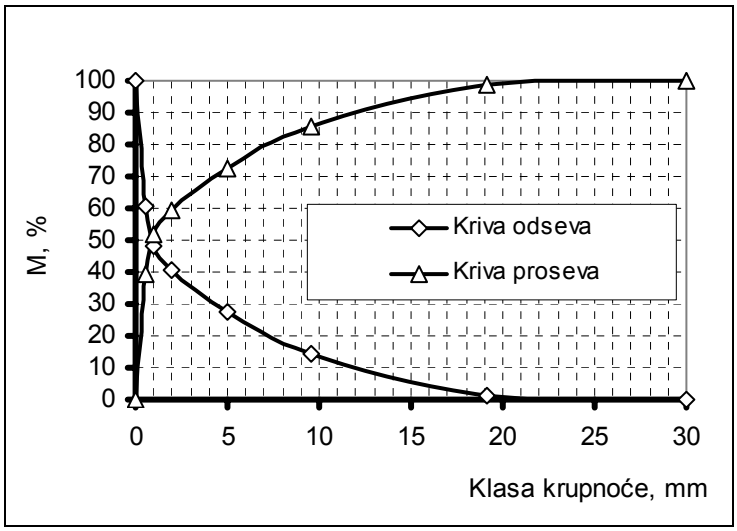
Na slici 1. je dat granulometrijski sastav dobijenog asortimana krečnjaka tj. klase krupnoće -20,0+0 mm.

Na tako pripremljenom materijalu su urađena dalja ispitivanja.

Određivanje sadržaja vlage polaznog uzorka krečnjaka je izvršeno je sušenjem uzoraka u laboratorijskoj sušari na tem-

peraturi od 105°C i merenjem do konstantne mase. Dobijena vrednost za sadržaj vlage u ulaznom uzorku litotamnijskog krečnjaka jeste 6,23%.

Određivanje nasipne mase dobijenog usitnjenog krečnjaka je vršeno merenjem mase uzorka u menzuri zpremine 1l. Dobijena vrednost je iznosila 1,39 t/m^3



Sl. 1. *Dijagram granulometrijskog sastava krečnjaka nakon usitnjavanja na potrebnu krupnoću -20,0+0 mm*

Mineraloškom analizom ispitivanih uzoraka krečnjaka ležišta "Dobrilovići" utvrđeno je prisustvo kalcita, kvarca, minerala glina, limonita. Kalcit je organogenog porekla, uglavnom kriptokristalast. Javljaju se fragmenti fosilnih ostataka. Kvarc je malo zastupljen. Krečnjak je slabo zaglinjen i limonitisan. [4].

Rezultati ispitivanja ***hemijskog sastava*** proizvoda usitnjavanja su prikazani u tabeli 2. [5].

Tabela 2. *Delimični hemijski sastav proizvoda usitnjavanja*

Element, jedinjenje	$CaCO_3$	$MgCO_3$	SiO_2	Fe_2O_3
Sadržaj, %	91,85	0,887	4,80	0,545

3.1. Ocena primenljivosti

Uporedni prikaz dobijenih rezultata ispitivanja krečnjaka ležišta “Dobrilovići“ i potrebnog kvaliteta krečnjaka za upotrebu u odsumporavanju dimnih gasova prikazan je u tabeli 3.

Tabela 3. *Uporedni prikaz dobijenih rezultata i zahtevanog kvaliteta krečnjaka za ODG*

Parametri	Jedinice	Stanje uzorka	Praškasti (rasuti) gips	Gipsane ploče	Krečnjak „Dobrilovići“
Slobodna vlaga	Težinski %	Po prijemu	≤5,0	≤5,0	**6,23**
Ukupni $CaCO_3$	Težinski %	Suv	≥89,0	≥94,0	**91,85**
Ukupni $MgCO_3$	Težinski %	Suv	≤4,0	≤3,0	**0,887**
Nerastvorni ostatak uključujući SiO_2 (kiselinski nerastvorni)	Težinski %	Suv	--------		**--------**
SiO_2	Težinski %	Suv	≤5,0	≤3,0	**4,80**
Fe_2O_3	Težinski %	Suv	---------	≤0,8	**0,545**
Inertne materije (uključujući $MgCO_3$)	Težinski %	Suv	≤11,0	≤6,0	**5,23**
Granulometrijska analiza	milimetri	Suv	-19,05+0	-19,05+0	**20,00+0**
Bondov radni indeks	kWh/T	Po prijemu	≤ 12,0	≤12,0	**8,09**

Iz rezultata datih u tabeli 3 može se videti da krečnjak iz ležišta „Dobrilovići“ zadovoljava uslove kvaliteata za dobijanje praškastog (rasutog) gipsa.

4. ZAKLJUČAK

U ovom radu prikazani su rezultati ispitivanja mogućnosti primene litotamnijskog krečnjaka, ležišta “Dobrilovići”, kod Loznice, u postrojenjima za odsumporavanje dimnih gasova u termoelektranama. Na osnovu poređenja rezultata dobijenih ispitivanjem i potrebnih karakteristika koje krečnjak treba da ispunjava, može se sa sigurnošću reći da uz minimalne korekcije, koje se jedino odnose na vlagu u uzorku (potrebno sušenje), krečnjak litotamnijskog porekla ležišta “Dobrilovići” u potpunosti odgovara za upotrebu u postrojenjima za odsumporavanje dimnih gasova. Primenom ovog krečnjaka u postupku odsumporavanja kao proizvod može se dobiti praškasti (rasuti) gips.

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LITHOTAMNIAN LIMESTONE FROM THE DEPOSIT "DOBRILOVIĆI" IN FLUE GAS DESULPHURIZATION BY WET PROCESS[**]

Abstract

This paper presents the results of investigation lithotamnian limestone from the "Dobrilovići" deposit for the use in flue gas desulphurization by wet process. According to the technological process conditions, FGD limestone should fulfill the certain criteria in order to be used for that purpose. In respect to those criteria, this paper investigates the chemical composition, bulk density, grain-size distribution and Bond work index (kWh/t). The results of these investigations have showed that limestone from "Dobrilovići" deposits, according to its physicochemical properties, is completely suitable for the flue gas desulphurization process in thermal power plants, as well as for disposable gypsum obtaining.

Keywords: *flue gas desulphurization by wet process, lithotamnian limestone, physicochemical properties, disposable gypsum*

1. INTRODUCTION

Within the National Program for Environmental Protection of the Republic of Serbia which was adopted in accordance with the Law on Environmental Protection, the measures for sustainable development and environmental management in the Republic of Serbia are planned for the ten-year period. One of the fundamental goals of environmental protection in the energy sector, in the period from

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2005-2014, is reduction the emission of sulphur oxides from large plants, such as the Thermal Power Plant ''Kostolac B'' and Thermal Power Plant ''Nikola Tesla A'' and ''Nikola Tesla B'', and the new thermal capacity on the Kolubara lignite of approximate power of 700 MW [1].

For the purpose of air protection, only flue gas conditioning devices for removal the particulate matter (electro filters) were installed, but no measures for reduction the sulphur oxides emission were taken. Concentrations in flue gasses exceed the allowed levels of domestic, as well as those of EU legislation several times [2].

The system of desulphurization consists of equipment for flue gas purification by wet process (flue gas cleaning) using the limestone suspension, which is carried out in a part of system called absorber. Flue gas cleaning is carried out by passing the flue gas stream into the absorber, into which the limestone suspension is introduced as spray or drops, facilitating the reaction of sulphur dioxide with calcium from limestone. It produces gypsum as suspension, which is then dewatered and taken to the storage or to the place where it is stored and prepared for future use. Purified flue gas is then discharged into the chimney, and from there into the atmosphere. Desulphurization process evidently requires large amounts of limestone which is brought from limestone mines [3]. Limestone which, used for desulphurization, is exploited and processed in queries of run-of-mine material in order to obtain the required quality. After that, it is transported to the limestone storages in desulphurization plants.

Gypsum suspension as a by-product of wet limestone desulphurization process is a potential raw material for gypsum obtaining. Gypsum quality depends on several factors, above all on the quality of input raw materials (limestone and water). In order to provide the required gypsum quality, it will be necessary to reconstruct the electro filter to reduce the concentration of particulate matter in flue gas.

This paper presents the results of investigation lithotamnian limestone from the "Dobrilovići" deposit for use in flue gas desulphurization by wet process. Investigation of moisture, chemical composition, bulk density, grain-size distribution and Bond work index are conducted.

2. EXPERIMENTAL

2.1. Material and Equipment

Starting sample was lithotamnian limestone from Dobrilović deposit near Loznica. Its grain-size distribution is present in Table 1.

Table 1. *Grain-size distribution of starting limestone*

Size class, mm	M, %
-200 + 100	34.00
-100 + 50	34.00
- 50 + 30	12.00
- 30 + 0	20.00
∑	100.00

The used equipment in the experiments was: laboratory ''Wedag'' jaw crusher, 5"x6"; laboratory ''Denver'' roll crusher, laboratory ''Kefama'' vibrating screen; laboratory ''Heraeus'' heating and drying oven; 1 l gauge glass; ''Perkin Elmer'' 703 atomic absorption spectrophotometer.

3. RESULTS AND DISCUSSION

Limestone starting sample was carefully crushed in the two-phase process, first by jaw crusher and after that by roll crusher. It was screened on the laboratory vibrating screen until size 100% -20mm was obtained. Namely, one of the requirements, regarding the quality of used limestone for flue gas desulphurization by wet process, is the size 19.05+0 mm.

Figure 1 presents the grain-size distribution of the obtained limestone assortment, i.e. size class -20.0+0 mm.

Such prepared material was further analyzed.

Measuring of moisture content. Measuring the starting sample moisture was performed by dewatering sample in a laboratory dryer at temperature of 105°C and measuring until the constant mass was obtained. The obtained value of moisture was 6.23%.

Bulk density of the obtained crushed was determined measuring the ample mass in 1 l gauge glass. The obtained value for bulk density was 1.39 t/m^3.

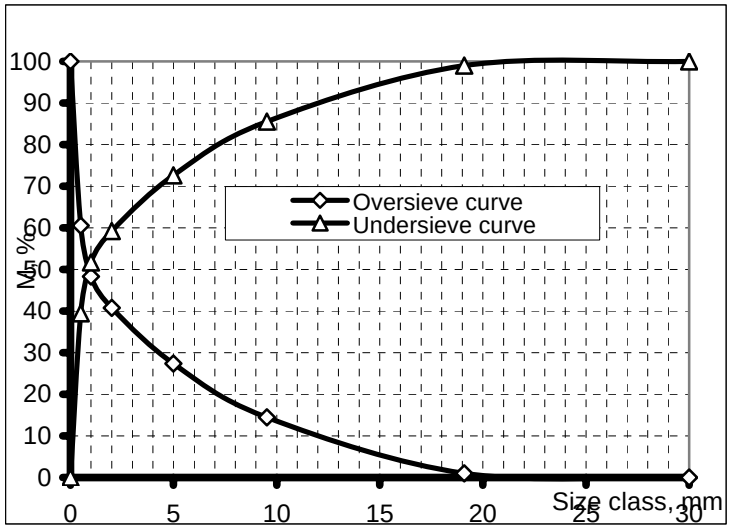

Fig. 1. *Diagram of limestone grain-size distribution after crushing into desired -20.0+0 mm size*

Mineralogical analysis of limestone samples from the ''Dobrilovići'' deposit: Mineralogical analysis showed the presence of calcite, quartz, and clay mineral limonite. Calcite was of organogenic origin, mostly cryptocrystalline. There were fossil residue fragments and minor quantities of quartz. Limestone contained small amounts of clay and limonite [4].

Results of ***chemical composition analysis*** of the crushed sample are present in Table 2 [5].

Table 2. *Partial chemical composition of limestone*

Element, compound	$CaCO_3$	$MgCO_3$	SiO_2	Fe_2O_3
Content, %	91.85	0.887	4.80	0.545

3.1. Applicability evaluation

Comparative overview the obtained results of limestone from the ''Dobrilovići'' deposit analyses and the required lime stone quality for the purpose of flue gas desulphurization are present in Table 3.

Table 3. *Comparative overview of the results and required limestone quality for FDG*

Parameter	Units	Reporting Basis	Disposable Gypsum	Gypsum Wallboards	Limestone "Dobrilovići"
Free Moisture	Weight %	As received	≤5.0	≤5.0	**6.23**
Total $CaCO_3$	Weight %	Dry	≥89.0	≥94.0	**91.85**
Total $MgCO_3$	Weight %	Dry	≤4.0	≤3.0	**0.887**
Insoluble matter including SiO_2 (acid insoluble)	Weight %	Dry	--------		**--------**
SiO_2	Weight %	Dry	≤5.0	≤3.0	**4.80**
Fe_2O_3	Weight %	Dry	---------	≤0.8	**0.545**
Total inert matters (including $MgCO_3$)	Weight %	Dry	≤11,0	≤6.0	**5.23**
Grain-size analysis	millimeters	Dry	-19.05+0	-19.05+0	**20.00+0**
Bond Work Index (BWI)	kWh/T	Ac received	≤12.0	≤12.0	**8.09**

The present results in Table 3 show that limestone from the ''Dobrilovići'' deposit meets the quality requirements for obtaining the disposable gypsum.

4. CONCLUSIONS

This paper presents the results of investigation the possibility of using lithotamnian limestone from the ''Dobrilovići'' deposit near Loznica in flue gas desulphurization systems in thermal power plants. Comparison the investigation results and requirements that limestone should meet, lead to a definite conclusion that lithotamnian limestone from the ''Dobrilovići'' deposit is completely suitable for the use in flue gas desulphurization systems with minimum corrections regarding sample moisture (necessary dewatering). Application of this limestone in desulphurization process can provide disposable gypsum product.

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