OPTIMIZING ENVIRONMENTAL SUSTAINABILITY: NOVEL APPLICATIONS AND ADVANCES IN FLUE GAS DESULPHURISATION TECHNOLOGY

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Abstract: *Flue Gas Desulphurisation (FGD) technologies play a pivotal role in mitigating environmental pollution stemming from coal-fired power plants, with wet limestone FGD standing out for its high desulphurisation performance and cost-effectiveness. The urgent need to reduce SO_2 emissions underscores the significance of wet limestone FGD systems, which have demonstrated remarkable efficacy in mitigating these emissions while maintaining relatively low operating costs.*

Flue gas desulfurization gypsum (FGDG) is a by-product of the flue gas desulfurization process in coal-fired power plants. Its chemical and physical properties make it suitable for various applications. However, despite its increasing production, its beneficial usage has declined over the past decade due to the presence of hazardous elements like arsenic, mercury, cadmium, lead, and selenium. Recent advancements in flue gas desulfurization technology have led to a reduction in these elements in "modern" FGDG, making it more attractive for reuse in other products.

This paper presents results from a new FGD plant meeting guaranteed values and explores novel and traditional FGDG applications with minimal environmental impact. The quality of the by-product gypsum, wastewater, and disposal gypsum was meticulously analyzed at the flue gas desulfurization plant situated at TPP 'Nikola Tesla A', on units DC2 and DC1. Specifically, the paper discusses the recycling of FGD gypsum for the removal of Pb(II), Cd(II) and other hazardous trace elements from wastewater.

By highlighting these applications and addressing research gaps, the aim is to promote greater reuse of FGDG and mitigate environmental concerns.

Key words: FLUE GAS DESULPHURISATION, GYPSUM, HAZARDOUS ELEMENTS, RECYCLING, SO_2 EMISSIONS

INTRODUCTION

Coal is a significant global energy source that plays a crucial role in power generation [1,2]. Due to its composition, which includes elements such as C, H, O, N, S, and hazardous trace elements (HTEs) like Hg, As, Cr, Cd, Ba, Mn, Pb, etc.coal-fired power plants are recognized as major contributors to air pollution, emitting pollutants such as NOx, SO_2, particulate matter (PM), and HTEs [3,4].

With increasingly stringent emission limits on conventional air pollutants such as NOx, SO_2, and PM, Serbia's power plants have increasingly installed air pollution control devices. These include electrostatic precipitators (ESPs) and wet flue gas desulfurization (FGD) systems. Numerous studies have shown that FGD systems not only capture SO_2 but also synergistically remove hazardous trace elements (HTEs) in both gaseous and particulate forms. Most of the HTEs removed from flue gas by FGD are retained in FGD gypsum, while some that remain in the flue gas are emitted into the atmosphere [5–8].

The most commonly used installation for reducing sulfur emissions from coal-fired power plants is the wet flue gas desulfurization (FGD) system using limestone. According to the Regulation on emission limit values of pollutants in the air from combustion plants ("Official Gazette of the RS", No. 05/16), the SO_2 removal efficiency should be ≥ 94%. During the process of removing SO_2, gypsum can be obtained as a byproduct, which finds further applications in construction, such as in the production of cement, wallboard, or as a soil conditioner. This helps to reduce waste material and disposal costs. The technological operations involved in the wet limestone flue gas desulfurization process are illustrated in the diagram shown in Figure 1.

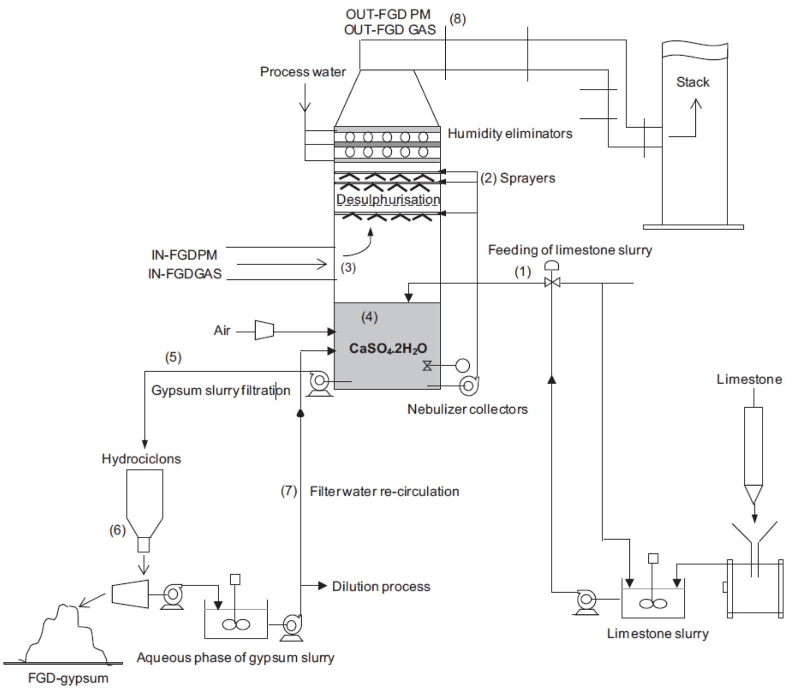

Figure 1, Sheme of Flue Gas Desulfurization (FGD) Plants

After separating solid particles in two electrostatic precipitators per unit, the flue gases are directed by a booster fan into two absorbers—one for units A3 and A4, and another for units A5 and A6. For the desulfurization process, water is pumped into the absorber, followed by a suspension of finely ground limestone obtained through wet grinding in a ball mill, along with the necessary air to provide oxygen for the reaction. In the reaction between limestone, water, oxygen, and sulfur dioxide from the flue gases, gypsum ($CaSO_4 \cdot 2H_2O$) and carbon dioxide are produced. The gypsum is removed from the absorber to undergo a thickening process and is then disposed of along with the ash. The cleaned flue gas is discharged from the absorber through a wet stack into the environment. During the wet desulfurization process at the plant, wastewater is generated, and its quality must be tested to ensure proper treatment and disposal.

Based on the basic nature, FGD gypsum can be utilized in construction and agricultural industry, such as production of cement, concrete and gypsum powder, wallboard manufacturing, fill material for the embankments, and additives for improving soil properties, etc. [9-12]. However, there is still a considerable number of FGD gypsum is disposal of landfills [13]. During the utilization or landfill, which may be related with heat treatment or chemical leaching, HTEs can be released from the FGD gypsum and bring great harm on the environment and human health. Thus, it is necessary to explore release characteristics of HTEs in FGD gypsum.

So far, limited research has been conducted on the reuse of FGD gypsum as an adsorbent for wastewater treatment, particularly for wastewater contaminated with heavy metals. Therefore, the primary objectives of this research were:

(i) To meticulously analyze the quality of by-product gypsum, wastewater, and disposal gypsum.

(ii) To assess the feasibility of using FGD gypsum for the removal of HTEs from wastewater.

By addressing these objectives and filling current research gaps, this paper aims to advocate for the broader adoption and sustainable reuse of FGD gypsum. This approach contributes to environmental conservation efforts and helps mitigate concerns associated with its disposal.

MATERIALS AND METHODS

The FGD gypsum, wastewaters, and disposal gypsum used for this study were collected from TPP 'Nikola Tesla A', specifically from units DC2 and DC1.

Gypsum obtained through the wet limestone flue gas desulfurization process must meet certain quality standards to be used for commercial purposes. The quality of the obtained gypsum was tested using the following methods: ASTM C 471M: 2020 Standard Test Methods for Chemical Analysis of Gypsum and Gypsum Products (Metric) for moisture content determination, EN ISO 10390:2022 (Soil, treated biowaste and sludge - Determination of pH) for pH value determination, ASTM C 471M: 2020 (Standard Test Methods for Chemical Analysis of Gypsum and Gypsum Products (Metric)) for gypsum purity, EN ISO 11885:2011 (Water quality - Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES) (ISO 11885:2007)) for water soluble MgO, EN ISO 11885:2011 for water soluble Na_2O, ISO 10304-1:2007 (Water quality - Determination of dissolved anions by liquid chromatography of ions - Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate) for Cl^- ions concentration, and Standard Methods: 4500-SO_3^{2-} B (Sulfite by Iodometry) for $CaSO_3$ x ½ H_2O.

The parameters used for testing the wastewater are as follows: ISO 10304-1:2007 (Water quality - Determination of dissolved anions by liquid chromatography of ions - Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate) was used for determining the concentration of Cl^-, the method for total suspended solids concentration involved filtration through glass fiber filters according to Water quality - Determination of suspended solids - Method, ISO 10523:2008 (Water quality - Determination of pH) was used for determining the pH value, and the photometric method DIN 38409-1 was employed for measuring COD. The concentration of HTEs in wastewaters was determined by inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer, USA).

EXPERIMENTAL ADSORPTION PROCEDURE

Batch adsorption experiments were carried out by exposing 0.1 g of FGD gypsum to 50 mL of wastewater in 250 mL Erlenmeyer flasks. For the kinetics studies, the contact time was varied from 0 to 180 minutes. All mixtures were shaken at 200 rpm in an air bath oscillator. After the shaking period, the mixtures were separated using a 0.22 µm membrane filter. The filtrates were then analyzed for the residual concentration of (HTEs) using Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

RESULTS AND DISCUSSION

The quality of gypsum

The chemical composition are shown in Table 1.

Table 1, The parameters of quality of byproduct gypsum

Sample ID	**pH**	**C (Cl^-)**	**c (Cl^-)**	**Moisture**	**c ($CaSO_4x2H_2O$)**	**MgO (water soluble)**	**MgO (water soluble)**	**Na_2O (water soluble)**	**Na_2O (water soluble)**	**c ($CaSO_3x1/2H_2O$)**
		mg/L	wt %	wt %	wt %	mg/L	wt %	mg/L	wt %	wt %
BG 01/24	7.29	7.51	0.009	9.57	98.61	64.0	0.006	29.8	0.003	0.064
BG 02/24	7.50	7.10	0.008	9.27	98.61	160.7	0.016	34.9	0.003	0.096
BG 03/24	7.46	7.35	0.008	9.16	98.81	135.2	0.013	32.1	0.003	0.032
BG 04/24	7.60	6.87	0.008	9.48	98.66	128.1	0.012	32.3	0.003	0.127
BG 05/24	7.32	7.52	0.009	8.08	98.71	107.1	0.011	35.2	0.003	0.064
BG 06/24	7.57	7.08	0.008	8.18	98.71	94.2	0.009	31.9	0.003	0.032
Guaranteed limit value	5-9	-	< 0.1	< 10	> 95	-	< 0.1	-	< 0.06	< 0.5

Table 1 presents the chemical properties and concentrations of various components in the samples analyzed. The pH values of all samples fall within the acceptable range of 5 to 9, indicating that the samples are stable and within the specified limits. Chloride concentrations ($C(Cl^-)$) are consistently below the guaranteed limit of 0.1 wt %, suggesting that chloride levels are well-controlled across all samples.

The moisture content in the samples varies, but all values are below the limit of 10 wt %, which is in line with the guaranteed specifications. The concentration of $CaSO_4 \cdot 2H_2O$ is above the limit of 95 wt % in all samples, demonstrating that the samples meet or exceed this requirement.

For water-soluble MgO, Na_2O, and $CaSO_3 \cdot 1/2H_2O$, the values in the samples are generally low, with most concentrations falling below the respective guaranteed limits. Specifically, the MgO (water soluble) and Na_2O (water soluble) concentrations are below 0.1 wt % and 0.06 wt %, respectively, while $CaSO_3 \cdot 1/2H_2O$ values are mostly under 0.5 wt %.

The data indicate that the samples are compliant with the specified limits for most of the parameters measured. The consistent pH values suggest stability in the samples chemical environment. The chloride, MgO, and Na_2O concentrations being well below the limit values reflect effective control of these potentially corrosive or reactive components.

The high moisture content in some samples (e.g., BG 05/24) is noted but remains below the maximum acceptable level, indicating that the samples are within the practical range of moisture content for handling and usage.

Although FGD gypsum (FGDG) has been used in the wallboard production industry for decades, research aimed at improving the quality of the product, assessing the environmental impact of FGDG in these boards, and exploring various methods for utilizing FGDG is ongoing. These results are consistent with previous studies, which have shown that effective control of chloride and soluble compounds is crucial for maintaining the quality and stability of similar materials. Currently, for FGDG to be incorporated into wallboards, it must meet the following basic requirements: $CaSO_4 \cdot 2H_2O$ content of over 92%, Moisture content less than 10 %, $CaSO_4 \cdot ½H_2O$ content of less than 0.5 %, chloride content less than 200 mg/kg, and the total content of K^+, Na^+, and Mg^{2+} should be less than 0.06 % [14].

The quality of wastewaters

Table 2 presents the measured quality parameters of the wastewaters, including Total Suspended Solids (TSS), Chemical Oxygen Demand (COD), Chloride (Cl^-), and pH. The results are compared against the guaranteed limit values.

Table 2, The parameters of quality of wastewaters

Parameter	**Number of measurements**	**Value**	**Garanteed limit value**
TSS (total suspended solid)	1	0.59	< 1,00 wt%
	2	0.61	
	3	0.57	
	4	0.60	
	5	0.62	
	6	0.55	
COD (chemical oxygen demand)	1	324	< 700 mg/l
	2	339	
	3	318	
	4	338	
	5	367	
	6	344	
Cl^-	1	542.6	< 20 000 ppm
	2	534.3	
	3	542.6	
	4	552.3	
	5	558.6	
	6	587.7	
pH	1	7.37	5 - 8
	2	7.21	
	3	7.12	
	4	7.23	
	5	7.16	
	6	7.14	

The measurements for Total Suspended Solids (TSS) ranged from 0.55 wt % to 0.62 wt %, all of which are below the guaranteed limit of 1.00 wt %. This indicates that the levels of suspended solids in the wastewater are well within acceptable limits.

Chemical Oxygen Demand (COD) values were observed to range from 318 mg/L to 367 mg/L. These values are consistently below the guaranteed limit of 700 mg/L, suggesting that the wastewater contains a relatively low level of organic pollutants. Chloride concentrations ranged from 534.3 ppm to 587.7 ppm, which are significantly below the guaranteed limit of 20 000 ppm. The pH of the wastewater samples ranged from 7.12 to 7.37, all of which fall within the acceptable range of 5 to 8.

In summary, the wastewater quality parameters meet the established limits, with low levels of TSS, COD, and chloride, and a stable pH.

Table 3, Concentration of HTEs in wastewater

Sample ID	**ww 09**	**ww 10**	**ww 11**	**ww 12**
As;(ppb)	13.966	6.788	7.627	8.591
Ba;(ppb)	17.470	18.160	19.551	20.072
Cd;(ppb)	10.947	7.417	7.544	8.000
Co;(ppb)	17.318	12.219	14.173	14.810
Cr;(ppb)	1.810	1.720	1.489	1.683
Cu;(ppb)	0.567	0.543	0.594	0.658
Mn;(ppb)	10,727.842	8,607.896	9,814.417	10,267.050
Ni;(ppb)	140.938	104.434	115.846	120.514
Pb;(ppb)	0.031	0.000	0.017	0.000
Sb;(ppb)	3.042	2.596	2.919	3.162
Tl;(ppb)	0.419	0.309	0.689	0.756
V;(ppb)	15.925	14.320	15.235	16.013

Table 3 presents the concentrations of various metals in the FGD wastewaters across different samples.

The concentrations of metals in the samples vary widely. Arsenic (As) levels range from 6.788 ppb to 13.966 ppb, with notably high levels observed across all samples, particularly in sample ww 09, which has the highest concentration. Barium (Ba) concentrations are consistently high, ranging from 17.470 ppb to 20.072 ppb, across all samples. Cadmium (Cd) concentrations vary between 7.417 ppb and 10.947 ppb, with particularly significant levels found in sample ww 09. Cobalt (Co) levels range from 12.219 ppb to 17.318 ppb, also indicating high concentrations throughout the samples. Chromium (Cr) concentrations are relatively lower compared to other metals, ranging from 1.489 ppb to 1.810 ppb, though they remain notable. Copper (Cu) levels are significantly low, ranging from 0.543 ppb to 0.658 ppb. Manganese (Mn) shows extremely high concentrations, ranging from 8,607.896 ppb to 10,727.842 ppb, indicating a predominant presence in the samples. Nickel (Ni) levels are also high, ranging from 104.434 ppb to 140.938 ppb. Lead (Pb) concentrations are very low, with some samples showing levels as low as 0.000 ppb. Antimony (Sb) concentrations are ranging from 2.596 to 3.162 ppb. Finally, thallium (Tl) levels are also relatively low, ranging from 0.309 ppb to 0.756 ppb. Vanadium (V) concentrations in the FGD wastewaters range from 14.320 ppb to 16.013 ppb. While vanadium levels are relatively high, they are lower compared to manganese and nickel.

The data indicate that the FGD wastewaters contain significant concentrations of certain metals, particularly manganese, nickel, arsenic, cobalt and barium. The exceptionally high levels of manganese, ranging in the thousands of ppb, and nickel, ranging from 104.434 ppb to 140.938 ppb, are particularly striking. These high concentrations suggest substantial contamination or accumulation of these metals in the wastewaters, which could have significant implications for both treatment processes and environmental impact, as both metals can be toxic at elevated levels.

Kinetics studies of adsorption

Tables 4, 5, and 6 present the results of *HTEs* adsorption on different types of FGD gypsum from three different power plants in Serbia.

Table 4, Results of HTEs adsorption on FGD gypsum from Power Plant Obrenovac C1 (A)

Sample ID	**As 75 (ppb)**	**Cd 111 (ppb)**	**Co 59 (ppb)**	**Cr 52 (ppb)**	**Cu 63 (ppb)**	**Ni 60 (ppb)**	**Sb 121 (ppb)**	**V 51 (ppb)**
A FGD 1-0'	11.62	9.84	18.04	1.80	1.14	156.15	3.16	16.01
A FGD 1-30'	11.21	8.80	18.00	1.68	0.75	150.80	2.87	15.76
A FGD 1-60'	11.14	8.72	17.33	1.66	0.73	147.08	2.77	15.56
A FGD 1-90'	11.00	8.71	16.99	1.58	0.73	143.66	2.76	15.14
A FGD 1-120'	10.98	8.52	16.93	1.55	0.71	143.66	2.75	14.93
A FGD 1-150'	10.20	8.00	16.06	1.54	0.71	139.61	2.68	14.57
A FGD 1-180'	8.71	7.58	18.00	1.49	0.66	120.32	2.58	14.10

Table 5, Results of HTEs adsorption on FGD gypsum from Power Plant Obrenovac C2 (B)

Sample ID	**As 75 (ppb)**	**Cd 111 (ppb)**	**Co 59 (ppb)**	**Cr 52 (ppb)**	**Cu 63 (ppb)**	**Ni 60 (ppb)**	**Sb 121 (ppb)**	**V 51 (ppb)**
A FGD 1-0'	11.51	8.90	17.91	1.69	0.83	151.07	3.16	16.01
A FGD 1-30'	11.26	8.87	17.27	1.59	0.74	144.70	2.91	15.59
A FGD 1-60'	11.03	9.00	17.61	1.64	0.76	149.39	2.83	15.59
A FGD 1-90'	10.89	8.81	17.90	1.68	0.78	150.35	2.81	14.87
A FGD 1-120'	10.75	8.43	16.71	1.55	0.75	141.79	2.79	15.79
A FGD 1-150'	10.32	8.33	16.95	1.57	0.74	144.91	2.73	14.48
A FGD 1-180'	9.93	8.00	14.88	1.68	0.63	120.51	2.66	14.86

Table 6, Results of HTEs adsorption on FGD gypsum from Power Plant Kostolac (C)

Sample ID	**As 75 (ppb)**	**Cd 111 (ppb)**	**Co 59 (ppb)**	**Cr 52 (ppb)**	**Cu 63 (ppb)**	**Ni 60 (ppb)**	**Sb 121 (ppb)**	**V 51 (ppb)**
A FGD 1-0'	9.98	9.24	17.04	1.60	1.04	146.88	3.16	16.01
A FGD 1-30'	9.90	9.48	16.90	1.57	1.27	146.58	2.76	14.56
A FGD 1-60'	9.78	8.34	16.59	1.51	0.71	138.97	2.72	14.79
A FGD 1-90'	9.77	8.28	16.72	1.55	0.71	141.07	2.69	14.65
A FGD 1-120'	9.70	8.16	16.78	1.53	0.71	139.89	2.65	14.79
A FGD 1-150'	9.31	7.79	15.91	1.48	0.68	134.97	2.62	14.71
A FGD 1-180'	8.59	8.06	14.81	1.58	0.67	120.55	2.54	14.12

Tables 4, 5, and 6 provide data on the adsorption of heavy trace elements (HTEs) on FGD gypsum from three power plants: Obrenovac C1, Obrenovac C2 (B), and.Kostolac (C). The results for Obrenovac C1 (Table 4) show similar trends to those observed in Obrenovac C2 and Kostolac. Across all three tables, there is a consistent decrease in arsenic (As) and antimony (Sb) concentrations over time. Variations in absolute values between plants suggest that factors such as gypsum composition or operational conditions may influence adsorption efficiency, though the overall effectiveness remains consistent.

However, these are initial findings, and further kinetic studies using adsorption models are still underway to better understand the adsorption dynamics and optimize the process. These results demonstrate the potential of FGD gypsum for heavy metal removal but require additional experimental validation.

CONCLUSION

The chemical analysis of the samples shows that they meet the guaranteed specifications for pH, chloride concentration, moisture content, and the levels of other soluble components. These findings underscore the effectiveness of the control measures in place and suggest that the samples are suitable for their intended use. The concentrations of metals in the FGD wastewaters are high for several elements, particularly manganese, nickel, arsenic, cobalt and cadmium. These findings highlight the need for stringent treatment and management practices to mitigate potential environmental and health risks. Compliance with regulatory standards is crucial to ensure the safe handling and discharge of these wastewaters.

Preliminary results indicate that FGD gypsum has potential as an effective adsorbent for heavy metals, evidenced by observed reductions in arsenic and cadmium concentrations over time. While these initial findings are promising, further experimental investigations and kinetic studies are necessary to validate these results and optimize the adsorption process.

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