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EXPERIMENTS ON THE POSSIBLE USAGE OF LIQUID INDUSTRIAL WASTES FROM A PAINT AND LACQUER FACTORY FOR FLUE GAS DESULPHURIZATION

In this paper, the complex solution of environment protection against flue gases (comprising sulphur dioxide) and alkaline industrial wastewater is provided. Industrial wastes from paint and lacquer factory were examined and their usage for sulphur dioxide absorption was determined. The combined method of the alkaline waste neutralization and flue gas desulphurization is proposed. The liquid wastes come from the POLIFARB SA plant in Wrocław.

1. INTRODUCTION

Industrial wastes produced in such plants as paint and lacquer factories, food industry factories, textile factories and so on become a serious problem for these plants. Such wastes are usually mixed with municipal wastes and then treated in sewage-treatment plants. The wastes often consist of organic components that come from production processes or from municipal wastes, thus they stabilize pH of solutions used for flue gas desulphurization (FGD) in range important to sulphur dioxide absorption. It would be preferred to use the alkaline wastes for FGD, especially if both sewage and flue gases are produced in the same plant. Development of combined method of simultaneous flue gas desulphurization and liquid industrial waste utilization would solve very important problem of their harmful effect on environment.

Power plants and local heat-generating plants have a major share in sulphur dioxide emission into the atmosphere. The essential problem for objects of this type is a proper choice of flue gas desulphurization methods. Commonly applied lime/limestone methods are useless because of the lack of place, investment costs and annual requirements.

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Industrial plants interested in flue gas desulphurization often produce alkaline wastes and a problem of their utilization is considered as equally important.

Based on the review of literature data it is suggested that some industrial wastes (e.g., from soda industry) can be used as SO_2 absorbents in wet methods of FGD.

Commonly applied FGD methods are based on a permanent capture of sulphur dioxide by calcium compounds. The majority of methods applied to industry are wet methods, often with modifications of both absorbent composition and installation arrangement to provide the best and inexpensive flue gas cleaning. Thus economical and environmental reasons have resulted in the possibility of using the waste absorbents for SO_2 removal.

The use of furnace waste for flue gas desulphurization has been discussed in several publications [1], [2]. Soda industrial wastes from open-hearth process and waste calcium carbide were examined [3], [4] in order to determine their absorbing properties and effectiveness in SO_2 removal.

Among the methods, which can be applied in small power objects and municipal heat-generating plants, dualalkaline method and its numerous modifications should be considered. The advantage of this method is the possibility of using waste absorbents, e.g., return water (supernatant) from settling ponds and hydraulic ash transport [5]. According to the experiments conducted the possibility of using alkaline solutions of calcium chloride and calcium nitrite was discussed [6]. The wet method of FGD, in which defecation mud and its supernatant are applied, has been presented in several papers [7], [8].

The necessity of minimizing the quantity of useless wastes discharged into the environment forces us to look for the method of utilizing atmospheric pollutants with industrial wastes, if possible. It can be often connected with wise interference in manufacturing and productive processes. Due to complex treatment it is possible both to clean flue gases and to use wastes hard to utilize, thus gaining real economical advantages.

Evaluation of usability of industrial wastes from paint and lacquer factory for SO_2 absorption and idea of development of flue gas desulphurization method using the wastes mentioned above were the aim of this paper. During experiments the wastes from the POLIFARB Wrocław SA were used.

2. CHARACTERISTICS OF WASTES

In the POLIFARB plant, SO_2 is formed during coal burning process in local boiler room where a heat used for manufacturing processes or heating is generated. The boiler room is equipped with four water boilers and two steam boilers with coal consumption of 5000 tonnes per year (in the future the coal consumption of 8000 t/a is expected). At full boiler capacity the emission of SO_2 is equal to 60 kg/h. Heat demand in the plant changes over the year, therefore the boilers work with variable

capacity, emitting different SO_2 amounts. They emit about 8 kg of SO_2/h in the summer and about 46 kg of SO_2/h in the winter.

According to investment plans in the POLIFARB, the FGD installation was accepted. It should be inexpensive, highly effective, easy to maintain and operate in a wide range of boiler capacity.

The authors of this paper designed the innovative project [9] allowing FGD. Its essence is based on using the alkaline wastes, a by-product of manufacturing processes.

Basic sources of wastewaters in the plant are as follows:

- department of resin synthesis,
- leaching plant,
- leakage from waste lagoon.

Along with industrial wastewaters, domestic wastewaters from the plant are mixed together in sewage pump station.

The experiments were carried out with the following solutions:

- post-leaching liquid wastes (+cistern washings periodically); several $\text{m}^3/24 \text{ h}$,
- raw wastes from settling pond consisting of industrial wastewater (+post-leaching liquid wastes periodically) and domestic wastewater (about 20%); $1200 \text{ m}^3/24 \text{ h}$,
- industrial wastewater and post-leaching liquid wastes added periodically without domestic wastes; about $400\text{--}500 \text{ m}^3/24 \text{ h}$,
- dispersion washings; several $\text{m}^3/24 \text{ h}$,
- leakage from waste lagoon transported to sewage pump station within the plant; about $2000 \text{ m}^3/24 \text{ h}$,
- dispersion, a product of the plant.

3. EXPERIMENTAL

3.1. RANGE OF THE EXPERIMENTS

The experiments consisted of:

- examination of primary wastes to determine their ability to absorb SO_2 ,
- modification of chosen wastes by mixing them in different ways and adding waste sodium hydroxide solutions and dispersion washings,
- determination of absorption efficiency of a chosen mixture of wastes with or without sodium hydroxide addition.

3.2. EXPERIMENTAL AND ANALYTICAL METHODS

The evaluation of the usability of liquid wastes for sulphur dioxide absorption was made by determining analytically their absorptive capacity (p).

Absorptive capacity was determined as the mass of SO_2 absorbed by volume unit of solution and expressed in kg/m^3 . Theoretical absorptive capacity (p_t) was expressed as the stoichiometric amount of SO_2 at the given solution alkalinity. The alkalinity was measured potentiometrically. Real absorptive capacity (p_r) was determined on the basis of SO_3^{2-} and SO_4^{2-} ion concentrations in solution obtained as a result of gaseous SO_2 flow through the solution. Sulphur dioxide in examined solutions was absorbed to pH values equal to 4.5 and 7. Concentration of SO_3^{2-} ions was measured iodometrically and that of SO_4^{2-} ions was determined as BaSO_4 by means of weight method.

3.3. THE EXPERIMENTS ON PRIMARY SOLUTIONS

The following solutions were chosen for examination:

1. Post-leaching liquid wastes.
2. Raw wastewater.
3. Industrial wastewater.
4. Dispersion washings.
5. Dispersion.

Theoretical SO_2 absorptive capacity of solutions was determined by the measurement of their alkalinity. The properties of primary solutions are presented in table 1.

Table 1

The properties of primary solutions

Solution	pH	Alkalinity (cm^3 0.1 M HCl per 1000 cm^3)	Amount of alkaline ions			p_t ($\text{kg SO}_2/\text{m}^3$)
			OH^-	CO_3^{2-} (kg/m^3)	HCO_3^-	
1	11.2	3580.0	5.4	1.2	—	22.91
2	7.85	46.0	—	—	0.28	0.29
3	8.4	35.0	—	—	0.21	0.22
4	6.85	149.0	—	—	0.87	0.91
5	8.9	2106.5	—	4.14	4.53	13.48

- 1 – post-leaching liquid wastes.
- 2 – raw wastewater.
- 3 – industrial wastewater.
- 4 – dispersion washings.
- 5 – dispersion.

Post-leaching liquid wastes (1) and dispersion (5) are characterized by the highest SO_2 absorptive capacity, while industrial wastewater (3) – by the lowest. Post-leaching liquid wastes comprise 12.72 kg of NaOH per m^3 , which strongly affects their alkalinity and SO_2 absorptive capacity.

3.4. MODIFICATION OF THE CHOSEN WASTEWATER COMPOSITION

Although industrial wastewaters have the lowest SO_2 absorptive capacity, they were chosen for further experiments. The most advantageous space arrangement of sewage system and localization of local boiler room became of crucial importance. The use of industrial wastewater would be the least energy-consuming. Wastes (3) were modified by addition of more alkaline solutions. The experimental data on modification of industrial wastes by means of post-leaching liquid wastes (1) is presented in table 2. The volume ratio of solutions in the mixture resulted from real amounts of wastes mentioned above. Constant pH value (about 4.5) of solutions at the volume ratios of 75:1 and 100:1 was observed.

Table 2

Industrial wastewater (3) modified by addition of alkaline wastes (1)

Run	Volume ratio of solutions	pH	Alkalinity (kg $\text{HCO}_3^-/\text{m}^3$)	p_t (kg SO_2/m^3)
1	50:1	10.4	0.71	0.75
2	75:1	9.95	0.48	0.50
3	100:1	9.45	0.42	0.44

Table 3 presents the experimental data on the solution (3) modified by means of dispersion (5). Modification of industrial wastewater (3) by addition of sodium hydroxide was also made (table 4). The change of sewage absorptive capacity was determined by means of NaOH addition in the range of 1.0–2.5 kg/m^3 . The experimental data on absorptive capacity of waste composition (3+1+4) at the volume ratio similar to that appearing in the plant and absorptive capacity of waste composition (3+1+4) with NaOH addition is shown in tables 5 and 6.

Table 3

Industrial wastewater (3) modified by addition of dispersion (5)

Run	Volume ratio of solutions	pH	Alkalinity (kg $\text{HCO}_3^-/\text{m}^3$)	p_t (kg SO_2/m^3)
1	5:1	8.7	2.54	2.64
2	10:1	8.65	1.37	1.44
3	15:1	8.67	0.96	1.00
4	20:1	8.6	0.735	0.77

Based on the values of theoretical SO_2 absorptive capacity, it is supposed that all SO_2 amounts emitted during coal burning process in the plant can be absorbed by modified solutions (table 6), provided that available amounts of wastes are used.

Table 4

Industrial wastewater (3) modified by addition of NaOH

Run	Addition of NaOH (kg/m ³)	pH	Alkalinity (kg HCO ₃ ⁻ /m ³)	<i>P_t</i> (kg SO ₂ /m ³)
1	1.0	11.15	1.58	1.66
2	1.5	11.3	2.32	2.43
3	2.0	11.5	3.15	3.30
4	2.5	11.55	3.9	4.09

Table 5

Industrial wastewater (3) modified by wastes of composition of (1+4)

Run	Volume ratio of solutions	pH	Alkalinity (kg HCO ₃ ⁻ /m ³)	<i>P_t</i> (kg SO ₂ /m ³)
1	100:1:1	10.35	0.472	0.796

Table 6

Waste composition of (3+1+4) modified by NaOH

Run	Addition of NaOH (kg/m ³)	pH	Alkalinity (kg HCO ₃ ⁻ /m ³)	<i>P_t</i> (kg SO ₂ /m ³)
1	1.0	11.9	1.8	1.89
2	1.5	12.1	2.65	2.78
3	2.0	12.25	3.29	3.46
4	2.5	12.3	4.18	4.38

3.5. EXAMINATION OF REAL ABSORPTIVE CAPACITY OF MODIFIED SOLUTIONS

The mixture of industrial wastewater (3), post-leaching liquid wastes (1) and dispersion washings (4) at the ratio of 100:1:1 and the same mixture with sodium hydroxide addition of 2.5 kg/m³ were examined. SO₂ absorption process was conducted to pH equal to 4.4 and 7 (table 7).

The values of real SO₂ absorptive capacity of the solutions modified by sodium hydroxide addition are two times lower than theoretical values. The absorptive capacity (0.46 kg/m³) of waste mixture determined without NaOH addition confirms that its absorptive ability is 8 kg of SO₂ per hour. It is equal to SO₂ amount emitted during the summer when the heat is generated only for the processing demands.

Table 7

SO₂ absorption in modified solutions

Run	Solution composition	pH (primary)	P_t (kg SO ₂ /m ³)	P_r (kg SO ₂ /m ³)	pH (secondary)	P_r/P_t (%)
1	3+1+4	10.3	0.496	0.459	4.4	92.5
2	3+1+4 +NaOH	12.65	4.38	2.540	4.4	58.0
3	3+1+4 +NaOH	12.65	3.87	1.260	7.0	32.6

The waste mixture (3+1+4) with sodium hydroxide addition (2.5 kg/m³) shows absorptive capacity of 2.54 kg of SO₂/m³ under the same process conditions as above. This means that about 51 kg of SO₂ can be absorbed per hour which exceeds SO₂ emission in winter.

3.6. SUMMARY OF EXAMINATIONS AND TECHNOLOGICAL CONCEPT OF FGD INSTALLATION

Our investigations should be continued and further experiments will allow us to determine:

- possibility of use of leakage from waste lagoon,
- effect of domestic wastewater addition to industrial wastewater on their absorptive properties,
- advantageous conditions for SO₂ absorption,
- recycling of post-absorption solutions in FGD unit,
- possibility of discharging the post-absorption solutions into local sewage treatment plant.

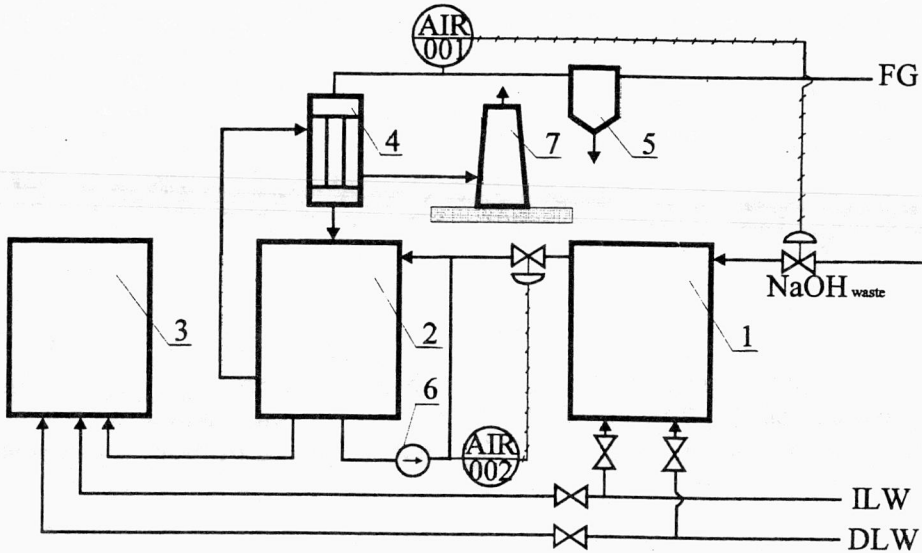
The scheme of the FGD installation, in which liquid wastes produced in the paint and lacquer plant are used for SO₂ absorption, is presented in the figure [9].

Flue gases are preliminarily precipitated in precipitators (5). Further they are cooled to the temperature of ca. 100°C in the heat exchanger (4) (type of flue gases/clean gases) by stream of cleaned gases of the temperature of ca. 50°C.

The mixture of industrial and domestic wastewaters is prepared in absorbent preparation system (1). Waste sodium hydroxide is added automatically, depending on SO₂ concentration (AIR 001).

Flue gases come into contact with absorption system (2), which consists of spray absorber.

Absorptive solution circulates in a closed loop: circulating pump (6), absorption system (2) until its absorptive capacity is used up. Mixture of wastes in system (1) is added automatically to system (2), depending on pH of circulating solution (AIR 002).



The scheme of the FGD installation

- 1 – absorbent preparation system, 2 – absorption system,
 3 – local sewage treatment plant, 4 – heat exchanger,
 5 – precipitator, 6 – circulating pump, 7 – stack,

FG – flue gas from boiler room, ILW – industrial liquid wastes,
 DLW – domestic liquid wastes, NaOH_{waste} – waste sodium hydroxide

Used post-absorptive solution is carried away from absorption system (2) to local sewage treatment plant (3). Cleaned gases flow to the stack (7).

4. CONCLUSIONS

1. The results obtained proved that the experiments conducted are necessary.
2. All sulphur dioxide amount emitted from local boiler room can be absorbed in the examined mixture of liquid wastes.
3. The addition of sodium hydroxide is necessary only at higher capacity of boilers, whereas flexible feeder regulation will be provided.
4. Sodium hydroxide added to the mixture of wastes is a by-product as well.
5. The concept proposed will bring real economical advantages for the plant.

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MOŻLIWOŚCI WYKORZYSTANIA ŚCIEKÓW POPRODUKCYJNYCH Z FABRYKI FARB I LAKIERÓW DO ODSIARCZANIA SPALIN

Przedstawiono kompleksowe rozwiązanie problemu ochrony środowiska przed szkodliwym działaniem gazów odlotowych (zawierających dwutlenek siarki) i alkalicznych ścieków poprodukcyjnych. Przebadano ścieki poprodukcyjne z fabryki farb i lakierów i określono ich przydatność do absorpcji dwutlenku siarki. Zaproponowano skojarzoną metodę unieszkodliwiania alkalicznych ścieków i odsiarczania spalin z wykorzystaniem powyższych ścieków w fabryce POLIFARB SA we Wrocławiu.

ВОЗМОЖНОСТИ ИСПОЛЬЗОВАНИЯ ПОСЛЕПРОИЗВОДСТВЕННЫХ СТОЧНЫХ ВОД ИЗ ЛАКОКРАСОЧНОГО ЗАВОДА ДЛЯ ОБЕССЕРЕНИЯ ГАЗОВ СГОРАНИЯ

Представлено комплексное решение вопроса охраны среды перед вредным действием газов сгорания (содержащих двуокись серы) и щелочных послепроизводственных сточных вод. Были исследованы послепроизводственные сточные воды из лакокрасочного завода и была определена их пригодность для абсорбции двуокиси серы. Предложен сопряженный метод обезвреживания щелочных сточных вод и обессерения газов сгорания вышеуказанных сточных вод на заводе Полифарб А.О. во Вроцлаве.

