

Application of aluminum-based coagulants for improving efficiency of flue gas desulfurization wastewater treatment in coal – fired power plant

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Abstract. Pollution released into the environment as the result of the combustion of energy fuels is a significant global threat. For instance, wastewater in coal–fired power plants is often heavily polluted by organic compounds, heavy metals and boron. Therefore, there is an urgent need for efficient flue gases and wastewater treatment. However, to be industrially implemented, the treatment processes have to be simultaneously effective and inexpensive. This research systematically studied the efficiency of inexpensive coagulation processes using aluminum-based coagulants applied to flue gas desulfurization (FGD) wastewater treatment. Additionally, the differences in the efficiency of total organic carbon (TOC) and chemical oxygen demand (COD) removal between sedimentation and coagulation processes were systematically studied. It was found that coagulation with the appropriate dose of PAX19XL coagulant achieved a satisfactory effect with significant boron removal and almost complete heavy metals removal. The polyelectrolyte use did not improve coagulation effectiveness and did not accelerate sludge sedimentation and volume decreasing. The detailed statistical analyses did not confirm the positive, pronounced effect of coagulation compared to sedimentation, although there were observed exceptions that should be considered separately. The results obtained suggest that inexpensive aluminum-based coagulants may be effective in improving the efficiency of flue gas desulfurization wastewater treatment in coal–fired power plants.

1 Introduction

Most of the world's energy is produced as the result of coal and petroleum combustion. In addition to carbon, the fuel used, contains a significant amount of impurities that remain in ash and slag or go into exhaust gases. These gases are treated before discharge to the environment. The purification involves removing solid particles, nitrogen oxides and sulfur oxides. Desulfurization of gases is most often carried out with a wet lime method,

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consisting of spraying the gases with a solution of lime milk or limestone [1-3]. The desulfurization product is calcium sulfate - gypsum [4,5], which is separated from the wastewater. The wastewater from flue gas desulfurisation (FGD) is characterized by high salinity, a high content of suspended solids, heavy metals and boron. The salinity can exceed even 30000 mg/L of chlorides and 2500 mg/L of sulfates (VI). The concentration of boron in the wastewater can be up to over 350 mg/L. The share of organic compounds in the total pollutant load is small. Wastewater from FGD is characterized by a differentiation in terms of qualitative and quantitative composition, depending on the type of fuel used, block load and hydraulic load of the installation. Many substances found in wastewater are compounds considered to be harmful to the environment. Most of these compounds persist in the aquatic environment and are toxic to aquatic organisms. In system power plants, most common wastewater treatment method used is based on the double coagulation with iron salts, initially at pH 6.0 and then 8.5, and complexation of metals using TMT-15 (15% aqueous solution of organic sulfide, trisodium 1,3,5-triazine-2,4,6-trithiolate). This technology is partially consistent with the Council Directive [6], Regulation of the Minister of the Environment [7], Regulation of the Minister of the Environment [8] and integrated and water permits obtained by the system power plant. The use of iron-based coagulants may not be sufficient to treat wastewater to the level described in the legal requirements. This problem is especially important in the case of heavy metal and boron. Therefore, there is a need to look for other wastewater treatment methods, that are efficient, inexpensive and applicable. The aim of this study was to determine the applicability and the efficiency of aluminium-based coagulants for the treatment of wet lime method FGD wastewater in a system power plant. In addition, we examined the credibility of total organic carbon (TOC) determination in a high salinity matrix using two TOC analyzers, whose operation methods differ significantly between each other as part of this work,.

2 Results

2.1 Raw wastewater

The parameters of raw wastewater are shown in Table 1. Raw wastewater is characterized by high turbidity, associated with a high content of easily settleable solids (ESS), in the which composition predominates gypsum. Inorganic contaminants dominate in the wastewater, both in the dissolved form and in suspension. Wastewater is characterized by high salinity (Table 1: content of chlorides 8595mg/L, sulphates 1920mg/L, conductivity 33.4mS/cm). Significant amounts of metals were determined. The concentration of Ni, Pb and Zn in raw wastewater exceeds 1mg/L, and Fe is in excess of 100mg/L (Table 1). B concentration was assessed as 340mg/L, whose source is combusted coal. The FGD wastewater from the system power plant has similar parameters to that described in the available literature [2,4,5].

2.2 Sedimentation

The results of coagulation and sedimentation are shown in Tables 2 and 3. Due to the large amount of ESS, sedimentation was very effective in FGD wastewater treatment. The use of the sedimentation alone, without the addition of coagulants, effectively removed suspensions (gypsum) and color. In addition, sedimentation decreased chemical oxygen demand (COD) from 395mg/L to 257mg/L (34.9% COD removal) and TOC from 47.73mg/L / 47.95mg/L to 44.42mg/L / 44.61mg/L (6.9% / 7.0% TOC removal). Thus, the

ESS was mineral in nature, and the organic compounds were found in the raw wastewater mainly in dissolved form. With the removal of the sediment, the content of boron decreased from 340mg/L in raw wastewater to 288mg/L in sedimented wastewater (15.3% removal). The use of sedimentation allowed to effectively decrease the content of Cr, Cu, Pb and Fe by at least 97.3% (Table 1). However, in the case of Ag, Cd, Zn and Ni, the content of these metals was reduced by 7.7%, 9.1%, 37.2% and 67.6%, respectively.

2.3 Coagulation

The use of the coagulation process decreased the COD values from 395mg/L to 244-282mg/L (28.6-38.2% removal) and TOC from 47.73mg/L / 47.95mg/L to 35.82 - 40.02 / 37.3 - 42.1 mg/L (16.2 - 25.0 / 12.2 - 22.2% removal). The largest COD removal was obtained using $Al_2(SO_4)_3$ at a 0.15mL/L dose and a pre-hydrolyzed coagulant PAX19XL at a 0.45mL/L dose. The COD value after the coagulation process was very similar to the raw wastewater after sedimentation. On the basis of COD values, it could be concluded, that it is impossible to choose the best type of coagulant or determine its optimal dose in terms of COD removal. The addition of polyelectrolyte does not improve the effectiveness of the coagulation process. But on the other hand, it could be concluded, that a minimal coagulant dose always ensures that the treatment process takes place.

Table 1. Parameters determined in raw wastewater

Parameter	Unit	Value	Legal requirement the integrated permit	Determination method
pH	-	6.74	-	PN-EN ISO 10523:2012
Conductivity	mS/cm	33.4	-	PN-EN 27888:1999
COD	mg/L	395	-	DIN 38409-41:1980-12
TOC (Shim-Pol)	mg/L	47.73	-	EN 1484:1999
TOC (API)	mg/L	47.95	-	EN 1484:1999
F ⁻	mg/L	13	25	PN-EN ISO 10304-1:2009
Cl ⁻	mg/L	8595	19000	PN-EN ISO 10304-1:2009
SO ₄ ²⁻	mg/L	1920	2900	PN-EN ISO 10304-1:2009
SO ₃ ²⁻	mg/L	3.46	-	EN ISO 10304-3:2001
NO ₃ ⁻	mg/L	232	-	PN-EN ISO 10304-1:2009
B	mg/L	340	180	PN-EN ISO 11885:2009
Ag	mg/L	0.039	-	PN-EN ISO 11885:2009
Cr	mg/L	0.447	-	PN-EN ISO 11885:2009
Cu	mg/L	0.61	0.5	PN-EN ISO 11885:2009
Ni	mg/L	1.226	0.5	PN-EN ISO 11885:2009
Pb	mg/L	2.018	0.5	PN-EN ISO 11885:2009
Cd	mg/L	0.308	0.4	PN-EN ISO 11885:2009
V	mg/L	1.489	-	PN-EN ISO 11885:2009
Zn	mg/L	15.9	2.0	PN-EN ISO 11885:2009
Fe	mg/L	129.6	-	PN-EN ISO 11885:2009

Coagulation with aluminium salts allows for the removal of dissolved organic compounds. The most effective organic compounds removal was obtained using coagulants from aqueous solutions of polyaluminium chloride, while the weakest treatment effect was using $Al_2(SO_4)_3$. The dose of the coagulant used did not have a significant impact on the efficiency of the process in the studied range.

The change in the pollutants' dispersion degree and the adsorption on the produced flocs, allowed the removal of organic compounds. Comparing the TOC values in treated wastewater, it was found that the use of coagulation allows for more than three-way more effective removal of organic pollutants in comparison to the sedimentation. The addition of flocculent in the coagulation process does not significantly affect the removal of organic compounds.

Usage of polyaluminium chloride coagulant modified by adding SiO_2 and Na^+ and Ca^{2+} ions, the did not improve the efficiency of the process. The lack of an additional effect can be explained by the high ionic strength of the solution and the fact that ESS may act as natural ballast for the sludge formed in the coagulation process. The metals in the suspended fraction are effectively removed in the form of a separated precipitate. The use of aluminium coagulants, regardless of the type or dose, allows the removal of most heavy metals from wastewater.

Table 2. Wastewater parameters after coagulation and sedimentation

Coagulant	Dose [mL/L]	AM91 3SH [mg/L]	COD [mg/L]	TOC Shim-Pol [mg/L]	TOC API [mg/L]	Conductivity [mS/cm]	SO_3^{2-} [mg/L]	SO_4^{2-} [mg/L]	Cl ⁻ [mg/L]	F ⁻ [mg/L]	NO_3^- [mg/L]
Sedimentation only	-	-	257	44.42	44.61	25.2	5.53	1916	8886	11	175
Al1019	0.3	-	263	37.27	37.3	25.9	1.71	1969	9017	11	200
Al1019	0.6	-	255	38.2	39.6	25.9	1.95	1948	8962	10	199
$Al_2(SO_4)_3$	0.075	-	252	39.83	41.9	25.3	3.78	1945	8740	12	174
$Al_2(SO_4)_3$	0.15	-	244	39.81	41.8	25.4	3.75	1908	8756	12	173
$Al_2(SO_4)_3$	0.3	-	253	39.54	42.1	25.0	3.64	1919	8603	12	172
$Al_2(SO_4)_3$	0.45	-	256	39.96	42	25.1	3.99	1911	8594	14	171
$Al_2(SO_4)_3$	0.6	-	250	40.02	41.1	25.1	3.59	1900	8596	11	188
$Al_2(SO_4)_3$	0.75	-	258	39.18	41.1	26.8	6.51	1890	9336	8	182
PAX19XL	0.075	-	254	38.57	40.4	25.3	3.84	1901	8718	9	184
PAX19XL	0.15	-	250	38.12	40	25.3	3.95	1909	8647	10	179
PAX19XL	0.3	-	262	38.66	40.1	25.6	4.26	1855	8789	9	182
PAX19XL	0.45	-	245	37.72	40	26.0	3.60	1992	8872	9	180
PAX19XL	0.6	-	263	37.65	39.9	26.3	3.38	1944	8990	9	178
PAX19XL	0.75	-	282	35.82	37.8	27.8	3.94	1856	9692	7	172
Al1019	0.075	6	261	37.94	X	24.9	3.43	1900	8436	10	153
Al1019	0.15	6	273	37.72	X	24.8	3.16	1893	8440	9	153
PAX19XL	0.075	6	X	37.71	X	24.8	3.53	1911	8478	11	153
PAX19XL	0.15	6	265	38.14	X	24.9	3.85	1891	8444	10	153

On the other hand, the Cr, Cu or Pb concentrations were comparable to those obtained as a result of the application of sedimentation alone. The use of aluminium coagulants improved the removal of Zn, Cd and Ni. In the case of these metals, the coagulation was used to remove about half of its content. However, which is interesting, when coagulant was supported by polyelectrolyte, the Zn removal efficiency was deteriorated.

The use of the aluminium salts coagulation was effective in removing B from wastewater, reducing its concentration from 340mg/L in raw wastewater to 145mg/L after coagulation PAX19XL in a 0.75mL/L dose (75.3% removal). The dissolved form of B dominates in raw wastewater. Only 15.2% of B is associated with the easily settleable solids (ESS). In coagulation with a modified, pre-hydrolyzed polyaluminium chloride (PAX19XL) the effectiveness of B removal depends on the coagulant dose. For $Al_2(SO_4)_3$, compared to pre-hydrolyzed coagulants, based on the dose of Al^{3+} , a worse process effect was obtained. In addition, it is not possible to determine the relationship between the effectiveness of removing B from wastewater and the dose of $Al_2(SO_4)_3$. Previous studies have shown, that during coagulation with iron salts at pH 6 and 9, B is weakly removed (maximum 25.0% removal) from this type of wastewater [9].

Table 3. Heavy metals and boron in wastewater after coagulation process

Coagulant	Dose [mL/L]	AM913 SH [mg/L]	Ag [mg/L]	B [mg/L]	Cd [mg/L]	Cu [mg/L]	Cr [mg/L]	Ni [mg/L]	Pb [mg/L]	V [mg/L]	Zn [mg/L]	Fe [mg/L]
Sedimentation only			0.036	288	0.280	<0.005	0.012	0.397	<0.010	x	9.99	0.092
Al1019	0.3	-	x	287	0.268	<0.005	0.012	0.396	0.015	0.016	5.37	0.210
Al1019	0.6	-	0.025	282	0.269	<0.005	0.015	0.396	0.011	0.015	x	0.146
$Al_2(SO_4)_3$	0.075	-	0.024	233	0.264	<0.005	0.013	0.358	<0.010	<0.005	9.73	0.331
$Al_2(SO_4)_3$	0.15	-	0.024	217	0.255	<0.005	0.015	0.351	<0.010	<0.005	8.10	0.306
$Al_2(SO_4)_3$	0.3	-	0.128	248	0.281	<0.005	0.018	0.384	<0.010	0.008	5.12	0.376
$Al_2(SO_4)_3$	0.45	-	0.023	245	0.276	<0.005	0.015	0.382	<0.010	0.009	x	0.863
$Al_2(SO_4)_3$	0.6	-	0.024	274	x	<0.005	0.018	x	0.014	0.007	x	x
$Al_2(SO_4)_3$	0.75	-	0.025	199	0.199	<0.005	0.014	x	<0.010	<0.005	5.134	0.051
PAX19XL	0.075	-	0.025	274	x	<0.005	0.014	x	<0.010	<0.005	x	0.167
PAX19XL	0.15	-	0.024	275	x	<0.005	0.015	x	<0.010	<0.005	x	0.138
PAX19XL	0.3	-	0.028	269	x	<0.005	0.014	x	<0.010	<0.005	x	0.262
PAX19XL	0.45	-	0.026	224	x	<0.005	0.014	x	<0.010	<0.005	x	0.073
PAX19XL	0.6	-	0.029	198	0.191	<0.005	0.013	0.311	<0.010	<0.005	x	0.063
PAX19XL	0.75	-	0.033	145	0.164	<0.005	0.009	0.230	<0.010	<0.005	5.800	0.013
Al1019	0.075	6	0.028	275	0.282	<0.005	0.012	0.397	<0.010	0.013	8.671	0.249
Al1019	0.15	6	0.028	277	0.281	<0.005	0.014	0.406	<0.010	0.008	7.927	0.845
PAX19XL	0.075	6	0.029	281	0.285	<0.005	0.013	0.399	<0.010	0.014	8.754	0.311
PAX19XL	0.15	6	0.027	281	0.286	<0.005	0.013	0.404	<0.010	0.012	8.244	0.258

Research on coagulation with aluminium and iron salts was carried out on similar FGD wastewater samples. It can be assumed that the positive effect of B removal is related only to the change in the form in which contamination occurs, depending on the pH, and

sorption properties of the resulting agglomerates using different coagulants. The resulting post-coagulation sludge was characterized by a low ability for sedimentation, the lowest in the case of $\text{Al}_2(\text{SO}_4)_3$. Only as a result of the use of polyelectrolyte, the resulting sludge was easier to sediment, but still the sedimentation rate was low. Regarding the practical application of aluminum coagulants for FGD wastewater treatment, an alternative method post-coagulation sludge removal, eg. filtration, should be considered. In the case of aluminum coagulants, the pollutants' (dissolved organic compounds, boron) adsorption process is usually important in the total removal effect. Shortening the contact time with the generated sludge affects the parameters of treated wastewater, which means that the share of the adsorption process in FGD wastewater treatment may be high. This finding confirms the comparison of the effectiveness of heavy metals and B removal in sedimentation and coagulation. Similar values of TOC and COD in both processes suggests that in coagulation, the dominant treatment process is the mechanical removal of pollutants as a result of gravitational sedimentation of the formed sludge.

3 Statistical analysis

In order to compare the values of the TOC parameter determined with the use of two analyzers: Shimadzu and GE, a non-parametric, independent of the statistical distribution, one-sided U Mann-Whitney test was performed. A pair of measurements were performed to check if the values could be considered as equivalent. The test showed that there is a statistical difference between the measurement results (the significance level $p = 0.002$). The TOC measurements with the GE instrument were usually higher by 1.66mg/L (the average of 14 measurement differences) than the TOC measurements made with the Shimadzu instrument. The ratios of the average difference in measurement between the TOC Shimadzu and TOC GE to the averages of measurements obtained using these analyzers were 4.3 and 4.1%, respectively. The standard deviation of TOC Shimadzu and TOC GE differences was 0.73mg/L, and the ratios of this deviation to the averages of TOC Shimadzu and TOC GE measurements were 1.9 and 1.8%, respectively. To compare the effect of the use of coagulation on the removal of COD with that of sedimentation, as well as with the joint use of coagulation and sedimentation, a non-parametric one-sided Wilcoxon test for one sample was performed. This test did not show a significant statistical difference between the COD values obtained after sedimentation and after coagulation. Similar results were obtained by the parametric one-sided Student's t test for one sample (significance levels were $p = 0.90$ and $p = 0.68$, respectively). The average COD value from all measurements for the process of combining coagulation and sedimentation was 258mg/L, and thus it was very close to the value of 257mg/L obtained for sedimentation alone. The standard deviation of COD differences in the two conditions of treatment process calculated for 17 different combinations of coagulants and doses were small and amounted to 9.7 mg/L. The statistical analysis did not confirm the positive, pronounced effect of coagulation compared to sedimentation, although there may be exceptions that should be considered separately.

4 Conclusion

The use of a coagulation using aluminium coagulants and the use of flocculants allows to achieve a satisfactory effect of FGD wastewater treatment, especially in case of heavy metal removal, up to complete removal of Pb, Cu, V, Cr and Fe. The sludge generated as a result of the process are characterized by low sedimentation ability. In the case of the possible implementation of aluminium coagulants in a real installation, a more efficient

post-coagulation sludge separation method, eg. filtration, should be applied. The use of polyelectrolyte did not increase the efficiency of COD and TOC, in the removal of heavy metal content in treated wastewater, as well as ion content. Based on the statistical analysis, it was found that there are no significant differences in the effectiveness of COD removal between the coagulation and sedimentation processes. In addition, it was confirmed that the results of determination of TOC with the use of both tested analyzers: Shimadzu TOC-L with ASI-L autosampler and GE Sievers Innovox with GE autosampler, were comparable and can be successfully used to evaluate the effectiveness of wastewater treatment processes in a system power plant. It should be emphasized that both devices were dedicated to determination of TOC in matrices with high salinity and high content of halides: structure resistant to corrosion and additional detector protection.

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