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The Effect of Fly Ash in Dewatering of Marble Processing Wastewaters

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***Abstract*—**In the thermal power plants established to meet the energy need, lignite with low calorie and high ash content is used. Burning of these coals results in wastes such as fly ash, slag and flue gas. This constitutes a significant economic and environmental problems. However, fly ash can find evaluation opportunities in various sectors. In this study, the effectiveness of fly ash on suspended solid removal from marble processing wastewater containing high concentration of suspended solids was examined. Experiments were carried out for two different suspensions, marble and travertine. In the experiments, $FeCl_3$, $Al_2(SO_4)_3$ and anionic polymer A130 were used also to compare with fly ash. Coagulant/flocculant type/dosage, mixing time/speed and pH were the experimental parameters. The performances in the experimental studies were assessed with the change in the interface height during sedimentation resultant and turbidity values of treated water. The highest sedimentation efficiency was achieved with anionic flocculant. However, it was determined that fly ash can be used instead of $FeCl_3$ and $Al_2(SO_4)_3$ in the travertine plant as a coagulant.

***Keywords*—**Dewatering, flocculant, fly ash, marble plant waste water.

I. Introduction

NATURAL stone exports, an important sector for Turkey, reached 2 billion dollars in 2017 [1]. While some of the exports are made of block marble, some of them are made of sized marble in marble plants. One of the most important problem in marble plant is the recovery of waste water used during marble cutting for reuse. For this, flocculants and coagulants are used in the plant.

In another sector, the number of thermal power plants are increasing day by day in order to meet the increasing electricity energy in Turkey. The number of active coal-fired thermal power plants in Turkey are 38 and 30 thermal power plants are under construction. In these plants millions of tons of fly ash are forming. Fly ash is a by-product arises from burning of the coal which is carried by flue gases or collected in cyclone and electro filter. Potential areas for the usage of fly ash vary from plastic fillers, high temperature ceramics to activated carbon and cement production [2], [3]. In Turkey there is not detailed data on the use of fly ash. In 2013, fly ash is mainly used in concrete and cement production in America (Fig. 1) [4].

By keeping the fly ash with the help of electro-filters in the funnels, the environmental pollution that it creates is also partially prevented. The fly ash also causes significant problems on transport and storage of the material. Due to these environmental problems, water and air quality, agricultural products, natural life, economical situation of the region and environmental beauty are unfavorable results [5], [6].

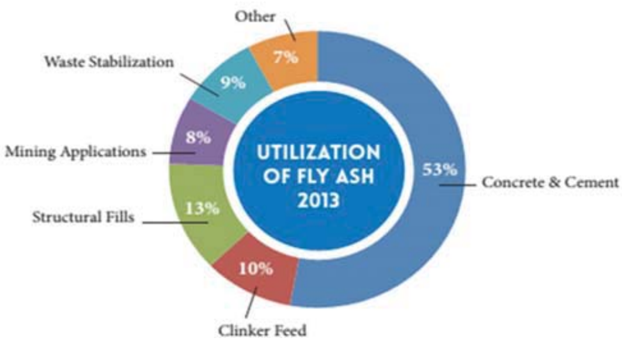

Fig. 1 Usage of fly ash in America in 2013

In the literature, it was carried out coagulation/flocculation experiments on the Trakya Cam Industry (Mersin-Tarsus) flotation plant waste. As a coagulant, Afşin-Elbistan fly ash and $Al_2(SO_4)_3$ have been used and it has been determined that fly ash can be used instead of $Al_2(SO_4)_3$ as a coagulant [7]. In another study, fly ash was used as coagulant for the removal of turbidity and organic pollution in the paper mill wastewater and determined that the fly ash was better than $Al_2(SO_4)_3$ and $FeCl_3$ [8].

In this study; coagulation/flocculation experiments were carried out on marble waste water from marble plants. The fly ash from the Seyitömer Thermal Power Plant as a coagulant was compared with commercially available $FeCl_3$, $Al_2(SO_4)_3$ and A130. Fly ash is low cost and its use as coagulant due to its chemical structure has been investigated. The main aim of this study is to evaluate both the fly ash formed in the thermal power plant and the problem of marble plants waste water.

II. Experimental

A. Material

Marble waste water consists of small marble particle and slime formed during cutting. In the experiments used waste water were taken from Polat Mining Company. One of the sample was travertine waste and other was calcite waste. Using 100 g sample, particle size analysis was performed from 20 µm to 212 µm by wet sieving. Particle size analysis showed that more than 75% of the travertine and calcite were in slime form (-20 µm) as seen in Table I.

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TABLE I
PARTICLE SIZE ANALYSIS OF THE TRAVERTINE AND CALCITE

Size Range (µm)	Travertine Weight (%)	Calcite Weight (%)
-150 +106	2,42	1,27
-106 +75	2,53	2,19
-75 +53	3,41	4,56
-53 +38	6,22	6,12
-38 +20	10,41	7,24
-20 +0	75,01	78,62
Total	100,00	100,00

Fly ash is a waste product of solid fuels combustion. It is a solid, fine and powdery material. Two different types of fly ash were used which are raw ash (Fly ash A) and separated ash (Fly ash B). Fly ash A was obtained with removing burned coal by cooling them in the water in the cyclone-type thermal plants. Fly ash B was obtained by sieving raw ash about 95% under 90 µm. Samples are taken from Kütahya/Seyitömer Thermal Plant. The particle size analysis of fly ashes A and B are given in Table II. 80% of fly ash A is under 204 µm while 80% of fly ash B is under 52 µm. The particle size of fly ash depends on type of coal and degree of grinding. Lignite coal ash has finest sized than hard coal.

TABLE II
PARTICLE SIZE ANALYSIS OF THE FLY ASH SAMPLES

Size Range (µm)	A Weight (%)	B Weight (%)
+212	17,95	-
-212+150	19,91	-
-150 +106	15,59	6,87
-106 +75	11,58	4,58
-75 +53	6,93	8,06
-53 +38	6,68	10,16
-38 +20	5,76	10,67
-20 +0	15,60	59,66
Total	100,00	100,00

The physical properties of fly ash vary depending on the nature of the fired coal. It is usually gray in color and the color becomes darker as the amount of unburned carbon in it increases [9]. The fly ash sample was characterized by XRF analysis and the results are presented in Table III. SiO_2 and Al_2O_3 were the major components in the fly ash.

$FeCl_3$ and $Al_2(SO_4)_3$ were used as coagulant and A130 was used as flocculants to compare the effects with fly ash. NaOH and HCl were used as pH regulators. Flocculants and coagulants were prepared from stock solution with distilled water and experiments were done dosing different concentrations for each to be worked before experiments.

TABLE III
CHEMICAL COMPOSITION OF FLY ASH SAMPLE

Element oxide	Amount (%)
SiO_2	54,49
Al_2O_3	20,58
Fe_2O_3	9,27
CaO	4,26
MgO	4,48
SO_3	0,52
K_2O	2,01
Na_2O	0,65
KK	3,01

B. Method

Experiments were carried out in 500 mL beaker with mechanical stirrer. Marble waste water suspension was prepared at 2% solid ratio. Firstly, suspension was pre-conditioned for 5 min at 850 rpm in order to obtain a well dispersed suspension. Then, $Ca(OH)_2$ and H_2SO_4 (Merck) solutions were used to adjust the pH. pH control was provided by a digital pH meter (Temp Meter 6230 pH meter) and added fly ash or coagulant/ flocculants into the suspension. After the suspension was stirred for 3 minutes at 100 rpm stirring and leaved settling. 10 ml of supernatant sample was taken from a fixed distance below the air-liquid interface at the end of the 30 minutes and turbidity was measured by a turbidimeter TB1 Portable Velp Scientifica. The sedimentation recovery of the processes was assessed using (1)

$$\text{Rec. (\%)} = [\ (T_0 - T_f) / T_0\ ] \times 100 \qquad (1)$$

where T_0 is the initial turbidity (NTU) of the suspension and T_f is the final turbidity of the supernatant after the process [10].

III. RESULTS

A. Free Settling of Travertine and Calcite

In order to determine the sedimentation behavior of marble suspensions without addition of any agent, turbidity and height of interface measurements have done (Fig. 2). Beginning turbidity of travertine was 1720 NTU while calcite was 2730 NTU. After 30 minutes, the turbidity of the travertine sample was 235 NTU and the calcite sample was 678 NTU. After 60 minutes, the height of interface of the travertine sample was settled to 129 mm and the calcite sample was settled to 236 mm.

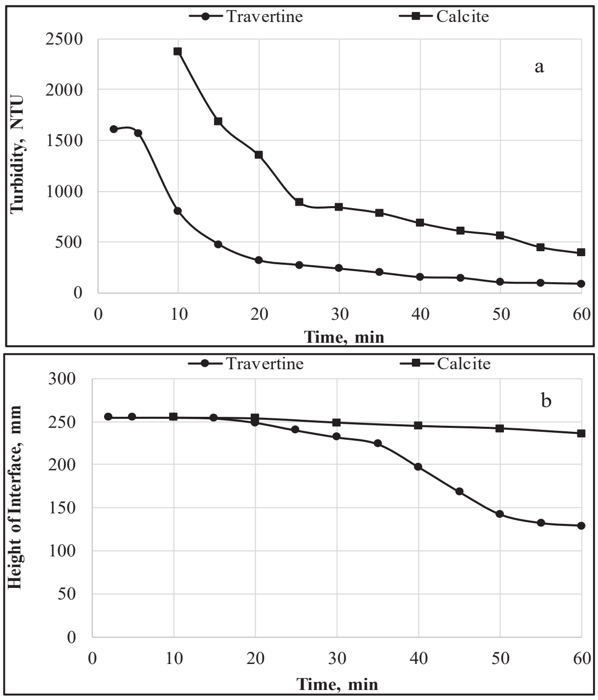

Fig. 2 Turbidity (a) and time dependent sedimentation (b) of marble suspensions

B. Optimization of Mixing Speed/Time and Settling Time with Fly Ash

To determine the effect of mixing speed, 2 gr of fly ash A added to suspensions and mixed 15 minute with different mixing speed. After mixing and 30 minutes settling time, turbidity of suspension measured. 100 rpm mixing speed gave the minimum turbidity values of 157 NTU for travertine and 403 NTU for calcite (Fig. 3 (a)).

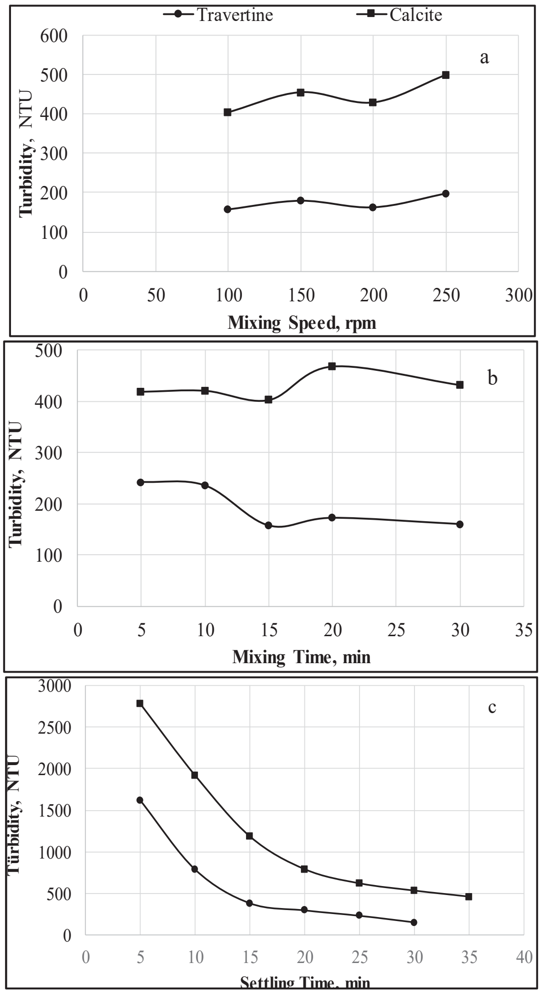

Fig. 3 Effect of mixing speed (a), mixing time (b) and settling time (c) of marble suspensions

The marble suspensions, which were added with 2 gr fly ash, were treated at different mixing times at optimized 100 rpm mixing speed. The optimum mixing time for both samples was determined to be 15 minutes giving the lowest turbidity value (Fig. 3 (b)).

To optimize settling time, at different times turbidity measurements were done. After 30 minutes, turbidity values of 152 NTU for travertine and 538 NTU for calcite were obtained (Fig. 3 (c))

C. Optimization Concentration of Fly Ash

In order to determine the sedimentation behavior of marble suspensions with addition of fly ash A and B, some experiments have done with different dosage (Fig. 4). While the lowest turbidity of travertine was obtained 78 NTU with the dosage of 12.5 g/L fly ash B, the lowest turbidity of calcite was obtained 318 NTU with the dosage of 12.5 g/L fly ash B.

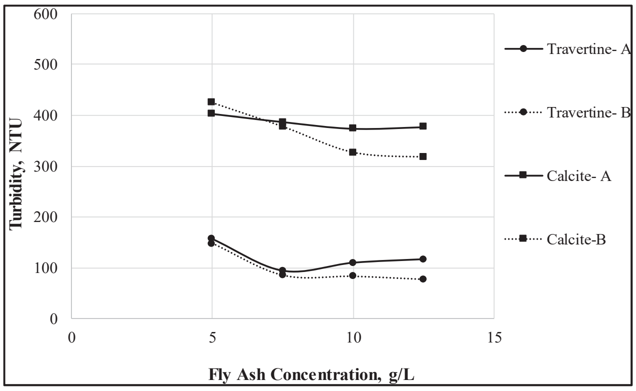

Fig. 4 Effect of fly ash concentration

D. Optimization of pH

Each coagulants and flocculants agent have its suitable pH range for coagulation and flocculation. Experiments were carried out at different pH by adding fly ash at the optimum dosages and conditions determined (Fig. 5). As the pH rises, turbidity of travertine was observed to be stable at about 100 NTU with fly ash A and B. On the other hand, calcite turbidity decreased as pH increased. Optimum pH values were found 8.3 (94 NTU) for the travertine with fly ash B and 11 (173 NTU) for the calcite with fly ash B.

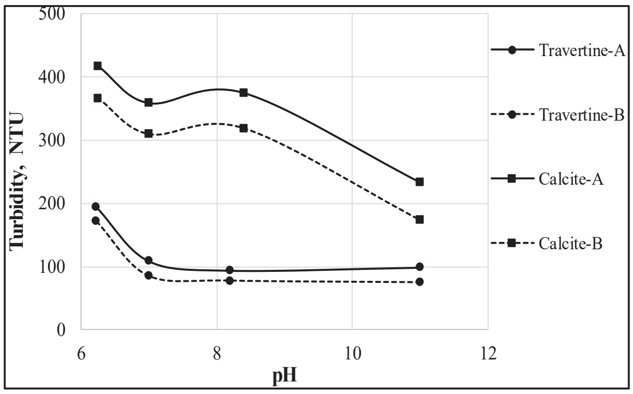

Fig. 5 Effect of pH

E. Effect of Flocculants and Coagulants on Turbidity Removal from Marble Suspensions

Experiments have done to determine effect of flocculants (A130-1 g/L) and coagulants ($FeCl_3$-5 g/L and $Al_2(SO_4)_3$-1 g/L). The results are given in Fig. 6. Travertine suspension turbidity was 143 NTU with 50 mg/L $FeCl_3$, 142 NTU with 30 mg/L $Al_2(SO_4)_3$ and 18 NTU with 20 mg/L A130. Calcite suspension turbidity was 303 NTU with 50 mg/L $FeCl_3$, 328 NTU with 30 mg/L $Al_2(SO_4)_3$ and 98 NTU with 20 mg/L A130.

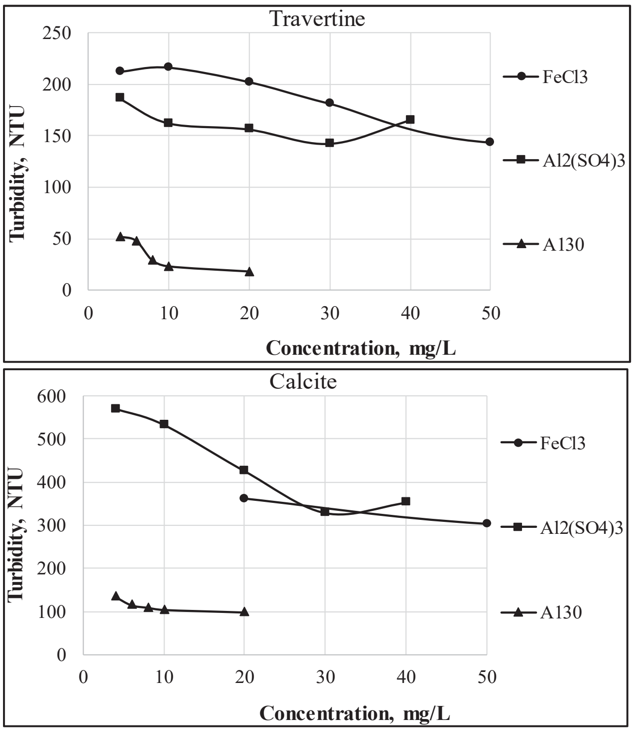

Fig. 6 Effect of flocculants and coagulants dosage

Table IV is given the optimum results obtained with the experiments. It is seen that fly ash B gave the good results than Fly ash A. This result should be because of the size distribution of the ashes. Fly ash B has more fine sized particle. Flocculants have formed from long chain polymers. Long chain polymers can be adsorbed on more than one particle by these chains and thus they are connected to each other by creating physical bridges between the particles. When the lowest turbidity is achieved with A130 for two different suspensions, fly ash A and B give the better results than $FeCl_3$ and $Al_2(SO_4)_3$ for travertine suspension. For calcite suspension turbidity was close between fly ash B-$FeCl_3$ and $Al_2(SO_4)_3$. In terms of suspension recovery, there is not much difference between recovery results. With the using of fly ash, which is a natural material, important recovery results have been obtained for waste evaluation.

TABLE IV
TURBIDITY CHANGE IN CONCENTRATIONS OF OPTIMUM VALUES IN TRAVERTINE AND CALCITE SUSPENSION

Material	TRAVERTINE			CALCITE		
	Optimum Con.	Turbidity (NTU)	Rec. (%)	Optimum Con.	Turbidity (NTU)	Rec. (%)
Fly ash A	6 gr/L	94	94,53	8 gr/L	374	86,30
Fly ash B	10 gr/L	78	95,46	10 gr/L	318	88,35
$FeCl_3$	50 mg/L	143	91,86	50 mg/L	303	95,31
$Al_2(SO_4)_3$	30 mg/L	142	91,74	30 mg/L	328	87,98
A130	20 mg/L	18	98,95	20 mg/L	98	96,41

IV. CONCLUSION

Fly ash utilization has grown over the years in many sectors. In this study, it was tried to eliminate the turbidity of marble waste water by using fly ash. The optimum mixing speed in calcite suspension was determined as 100 rpm (403 NTU) while it was determined as 100 rpm (157 NTU) in the travertine suspension. The best raw ash (Fly ash A) dosage in the travertine suspension was found to be 3 gr (94 NTU) and the separated ash (Fly ash B) dosage was 5 gr (78 NTU). The best raw ash (Fly ash A) dosage in calcite suspension was determined to be 4 gr (374 NTU), the separated ash (Fly ash B) dosage was 4 gr (318 NTU). The best pH value in the travertine suspension was 8.3 and the pH value in the calcite suspension was 11. In coagulation experiments, the best result of travertine suspension (140 NTU) was found in the addition of 100 mg/L $FeCl_3$, and the calcite suspension (128 NTU) was also found in the addition of 200 mg/L $FeCl_3$. In the flocculation experiment, the best result of the travertine suspension (18 NTU) was detected with the addition of 20 mg/L A130 and the calcite suspension (98 NTU) was obtained with the 20 mg/L A130. The results obtained with this work showed that fly ash can be used for dewatering.

Most fly ash obtained from thermal power plants contains sufficiently iron and aluminum oxide. Iron and aluminum oxide weight ratios of fly ash are suitable for producing a complex coagulant [11]. Using of fly ash as coagulant will be less costly than other manufactured products and will protect natural resources without the use of iron and aluminum oxides. The experimental results also show that the fly ash helps to accelerate the dewatering and the settlement of the marble processing wastewaters.

REFERENCES

[1] IMIB, *Yıllık bazda maden ihracat verileri*, Istanbul Maden İhracatçıları Birliği, Istanbul 2017.
[2] T.A. Gary, M.T. Perry, P.W. Conred, “Management of coal waste disposal for reduced environment impacts and for increased profits,” SME Preprint, pp. 94–127, 1994.
[3] N. E. Altun, C. Xiao, J. Y. Hwang, “Separation of unburned carbon from fly ash using a concurrent flotation column,” Fuel Processing Technology, 90, 1464-1470, 2009.
[4] ACAA, *American Coal Ash Association,* USA, 2018.
[5] M. Tokyay, K. Erdoğdu, “Türkiye termik santrallerinden elde edilen uçucu küllerin karakterizasyonu,” TÇMB, Ankara, 1998.
[6] S. Aytekin, “Uçucu küllerinin killi zeminlerin islahinda kullanimi,” Çukurova Üniversitesi Fen Bilimleri Ens. Y. Lisans Tezi, Adana, 2009.
[7] O. Bayat, B. Bayat, H. Vapur, V. Arslan, M. Uçurum, “Cam sanayi atıklarının uçucu kül ile koagülasyonu,” Mad. Dergisi, 44/3:19-24, 2005.
[8] L. Bingtao, L. Zhang, “Experimental Study on Wastewater Treatment by Fly Ash Coagulant,” International Conference on Electric Technology and Civil Engineering, China, 2011.
[9] H. Erşan, “Uçucu küllerin siltli zeminlerin kayma mukavemeti üzerine etkisi,” İTÜ Fen Bilimleri Enstitüsü, Y. Lisans Tezi, 75 s., İstanbul, 1996.
[10] A. Ozkan, M. Yekeler, “Coagulation and flocculation characteristics of celestite with different inorganic salts and polymers,” Chem. Eng. Process 43:873–879, 2004.
[11] M. Fan, R. C. Brown, J. V. Leeuwen, M. Nomura, Y. Zhuang, “The kinetics of producing sulfate-based complex coagulant from fly ash,” Chemical Engineering and Processing 42:1019/1025, 2003.