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Use of Waterworks Sludge, Ferric Chloride and Alum for the Treatment of Papermill Wastewater

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Water treatment works using coagulation/flocculation in the process stream will generate a waste sludge. This sludge is termed as ferric, alum or lime sludge based on the coagulant primarily used. The work in Adana, Turkey uses ferric chloride. The potential for using this sludge for the treatment of corrugated paper mill wastewater by coagulation has been investigated. Two main parameters were investigated namely chemical oxygen demand (COD) and total suspended solids (TSS). The sludge acted as a coagulant and low COD and good TSS removal efficiencies were obtained. The optimum condition works at pH of 6 and a sludge dose of 500 mg/L. The efficiency of sludge was also compared with alum and ferric chloride for the paper mill industry wastewater.

Key Words: Papermill effluent, Chemical treatment, Water treatment, Ferric sludge.

INTRODUCTION

Pulp and paper industry is one of the most common industries all over the world that uses significant amount of fresh water and produces substantial amount of waste products. Although virgin pulp is the main source of paper, however, use of recycled or secondary fibre is also getting more common due to the increasing consumer demands and also lack of sources. Therefore, the number of mills using recycled fibre from post-consumer sources is on a steady increase. For example in USA nearly 50 per cent of all papermills rely totally on secondary fibre[1]. A cleaning process is applied to recycled paper in order to remove dirt, glue, starch etc. depending on the end product. For white grades, such as newsprint, the recycled fibre is de-inked using flotation, followed by washing and screening. Soluble components such as starch are removed in the wastewater[2].

Application of the chemical or the physico-chemical treatment is common practice to many industrial wastewaters prior to discharge to sewer system or biological treatment in order to achieve satisfactory degree of treatment. Coagulation is one of those chemical treatment methods for the clarification of industrial wastes containing dissolved organic matter or colloidal matter. Wastewater from papermill may contain significant amount of dissolved or suspended solids (Table-1). In fact, a recent survey[2] within the industry in the UK has shown that COD values can be as high as 11,000 mg/L. Due to the high COD and TSS content, suitable method(s) must be applied to the wastewater from this industry in order to achieve desired wastewater treatment. The main treatment process for the wastewater from this industry is primary clarification and if necessary followed by biological treatment. In some cases further treatment or colour removal is also applied depending on the discharge consent[2]. Primary clarification may be achieved by either sedimentation or flotation. Within the papermills surveyed in the UK, sedimentation was the preferred option. These units achieved a high removal of suspended solids,[2] on an average > 80%. During primary treatment chemicals are used and most commonly they are known as coagulants. However, use of these chemicals means extra cost for the industry depending on the volume of the wastewater and the concentration of the pollutants.

TABLE-1
UNTREATED EFFLUENT LOADS FROM PAPER MANUFACTURE[20]

Paper type	Kg/tonne of product	
	Suspended solids	5-day BOD*
Fine papers	22–45	7–18
Book or publication papers	22–45	9–22
Tissue paper	13–45	4–13
Boxboard	22–30	9–18
Corrugated board	22–30	11–26
Newsprint	9–26	4–9
Insulating board	22–45	67–70

*Biochemical oxygen demand.

The use of these coagulants is also common practice in water treatment process in order to remove turbidity and other materials from raw water to make it potable. Hydrolysing metal salts or synthetic organic polymers are added in the water treatment process to coagulate suspended and dissolved contaminants and this operation yields relatively clean water. Most of these coagulants and the impurities settle to the bottom of the settling basin where they become part of the sludge, which requires disposal. This sludge is referred to as alum, iron or polymeric sludge according to which primary coagulant is used and these wastes account for approximately 70 per cent of the water plant generated wastes[3].

In Europe alone, several million tons of waterworks sludge are produced every year and it is forecasted that this figure will be doubling by the next decade[4, 5]. Waterworks sludge is classified by the current EU legislation[6] as "nonhazardous" and thus used in land filling together with municipal solid wastes[7]. However, in some countries cost of sludge disposal increased. For example, in the UK, due to the introduction of the Environmental Protection Act, water treatment sludge is now considered as an industrial waste and accordingly it has to be disposed to a registered landfill site[8]. Due to the vast amount produced in Europe alone and because of the tighter environmental regulations, water companies have been seeking cheaper and cost effective options in order to minimise sludge removal cost. Therefore, there have been significant researches on waterworks sludge. Coagulant recovery is now considered one such option in order to reduce sludge disposal cost. Aluminium and iron hydroxides in the clarifier sludge show good solubility in acidic as well as in alkaline media due to their amphoteric nature[9]. Therefore, it is possible to recover metal hydroxides from sludge suspensions by modulating pH system[7]. However, it was already reported that the purity of the coagulants recovered may not be sufficient to justify their reuse in the potable water treatment process; yet the process is also expensive and laborious[7, 9–11]. The use of recovered coagulants from waterworks sludge on wastewater treatment was also reported[8]. It was also reported that commercial coagulants performed better than recovered coagulants and they suggested blending it 50 : 50 with commercial coagulant[8].

In addition to coagulant recovery from the waterworks sludge, there have been also some researches on the use of waterworks sludge as a coagulant or as an adsorbent. Chu[12] has used alum sludge for the removal of heavy metals through coagulation process and reported high lead removal without adding fresh alum. Chu[12] has also used alum sludge for the coagulation of various dyestuffs and reported that alum sludge is effective in removing hydrophobic dyes in wastewater while simultaneously reducing fresh alum dosage, from which one-third of the fresh alum can be saved. Huang and Chiswell[11] have also used spent alum sludge for phosphate removal and found that alum sludge reduced phosphate level in wastewater significantly. In a recent study, it was demonstrated that the use of ferric sludge for the treatment of textile wastewaters and various dyestuffs as a coagulant was very effective and comparable with original coagulants[13]. It was also reported that ferric sludge was efficient adsorbent for Acid Blue 40, Basic Violet 16 and Direct Blue 71[13].

This paper reports the results of an examination of the coagulation effect of iron-based waterworks sludge on wastewater from papermill using totally post-consumer recycled paper.

EXPERIMENTAL

The wastewater was obtained from a local papermill factory in Adana city. This papermill uses totally mixed recycled paper (post-consumer secondary fibre) without deinking and produces corrugated type of paper. The composition of the wastewater is given in Table-2. The waterworks sludge was obtained from a potable water treatment plant in Adana city. This plant takes water from the river Ceyhan. Water quality of the river is variable; however, general water quality characteristics are shown in Table-3. The water treatment plant uses $FeCl_3$ (*ca.* 800 kg/day) as a coagulant for the removal of colloidal matter and turbidity. The sludge was obtained from the sedimentation tank as slurry, which had a pH of 8.6, a total suspended solids concentration of 32.48 g/L and volatile suspended solids concentration of 2.082 g/L. Its iron concentration was 207 mg/g. In addition to the sludge, alum $[Al_2(SO_4)_3 \cdot 18H_2O]$ and ferric chloride $[FeCl_3 \cdot 6H_2O]$ were also used for comparison. The optimum pH for alum was 6; for ferric chloride it was 8. All parameters were carried out according to standard methods[14].

The jar tests (Phips and Birds) which were used to examine the coagulation properties of the sludge, alum and ferric chloride, were done in duplicate and the results reported as means. In each test coagulants were added to wastewater (900 mL) and mixed rapidly (100 rpm) for 2 min. After this they were stirred more slowly (60 rpm) for 30 min. The flocs which had been formed were then allowed to settle for 30 min. Supernatant (300 mL) was then siphoned off for analysis. The initial pH adjustments were made with sulphuric acid (1.0 M) or sodium hydroxide (1.0 M) before the addition of the coagulant and re-adjusted during the rapid mixing stage. The dose of waterworks sludge was quantified by the dry weight of total suspended solid in the slurry at 105°C.

TABLE-2
WASTEWATER CHARACTERISTICS

Parameters	Sample 1	Sample 2
pH	7.60	7.59
COD (mg/L)	3536	2648
Filtered COD (mg/L)	2342	1836
BOD-5 (mg/L)	1489	1058
TSS (mg/L)	1628	918

TABLE-3
A GENERAL WATER QUALITY CHARACTERISTIC OF RIVER CEYHAN AT THE POINT WATER TREATMENT PLANT TAKES WATER

Parameters	
pH	8.1
Colour (Pt-Co)	170
Turbidity (NTU)	110
Dissolved oxygen (mg/L)	9
Suspended solids (mg/L)	210
COD (mg/L)	9
Total dissolved matter (mg/L)	590
Hardness mg/L $CaCO_3$	130
Total alkalinity mg/L $CaCO_3$	200
Bicarbonate (mg/L)	244
Iron (mg/L)	12.6
Nitrate (mg/L)	6.2

RESULTS AND DISCUSSION

The effect of varying the pH on the COD and TSS removal by coagulation is shown in Fig. 1. A sludge dose of 3000 mg/L was used and the data are based on settlement time of 30 min. High removal efficiencies were obtained at a pH value of 6 for COD and TSS. However, at higher pH values there was a deterioration in efficiency in terms of COD removal. For TSS removal, on the other hand, increasing pH is accompanied with only slight increase. This increase was negligible and also impractical due to addition of base in order to adjust pH value to higher pH values. Therefore, for the subsequent work, a value of pH 6 was chosen which was found as an optimum pH for the corrugated papermill wastewater.

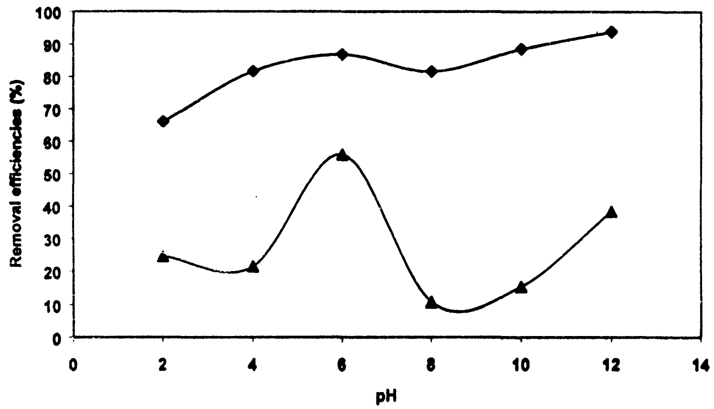

Fig. 1. COD (▲) and TSS (◆) removal by waterworks sludge in relation to pH.

Alum and ferric chloride are the commonly used coagulants for the chemical treatment of pulp and papermill wastewaters[15–17]. In this work, alum and ferric chloride were also used. The effect of coagulant dose was then examined and compared with alum and ferric chloride. Results of the comparison of the maximum removal efficiencies with those obtained by ferric chloride and alum are given in Table-4. All the data are for the optimum pH values (6 for sludge, 8 for ferric chloride and 6 for alum) and settlement period of 30 min.

TABLE-4
MAXIMUM REMOVAL EFFICIENCIES OBTAINED BY WATERWORKS SLUDGE AND COAGULANTS

Parameters	Sludge		Ferric chloride		Alum	
	Removal (%)	Dose (mg/L)	Removal (%)	Dose (mg/L)	Removal (%)	Dose (mg/L)
COD	43	1500	44	500	46	2000
TSS	87	2000	93	1250	95	1250

The comparison of the effect of coagulant dose on COD removal from the papermill wastewater is presented in Fig. 2. It shows that the sludge could achieve an efficiency which was comparable to that obtained with both alum and ferric chloride. Better results obtained with alum compare to other coagulants. COD removal rates of waterworks sludge did not exceed 43% even under the dose of 2000 mg/L. At low coagulant concentrations (250–500 mg/L) alum and ferric chloride achieved better COD removals than waterworks sludge. However, more than 1000 mg/L of waterworks sludge were needed in order to achieve comparable rates with alum and ferric chloride. In fact higher coagulants dose did not brought about better COD removal. These low COD removal rates during primary treatment were already reported by various researchers that unlike primary settlement in domestic wastewater treatment at papermills there is little removal rate of organic material[2, 16].

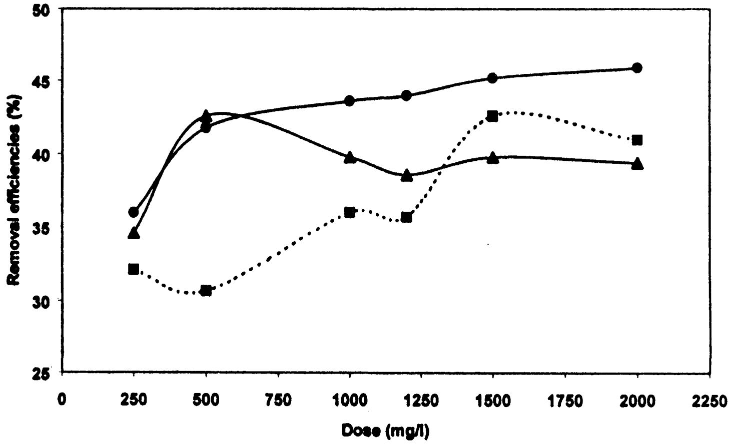

Fig. 2. COD removal from the wastewater by waterworks sludge (■), ferric chloride (▲) and alum (●).

Papermill wastewaters contains significant amount of suspended solids. Therefore in order to eliminate some part of these suspended solids primary clarification is used. During this stage, sedimentation or dissolved air flotation are used. However, sedimentation was the preferred option within the papermills surveyed in the UK and more than 80% of the suspended solids can be removed during primary clarification[2]. Similar suspended solids removal was also reported in a survey of plants treating the wastewaters from papermills in Finland showing that the primary clarifiers removed more than 80% of the suspended solids[18]. Before settlement, chemicals or most commonly known coagulants must be added in order to achieve satisfactory TSS removal. Therefore, the effect of coagulant dose of waterworks sludge was also examined and compared with alum and ferric chloride for TSS removal. Results obtained for TSS removal from the corrugated papermill wastewater are presented in Fig. 3. It shows that the waterworks sludge was also

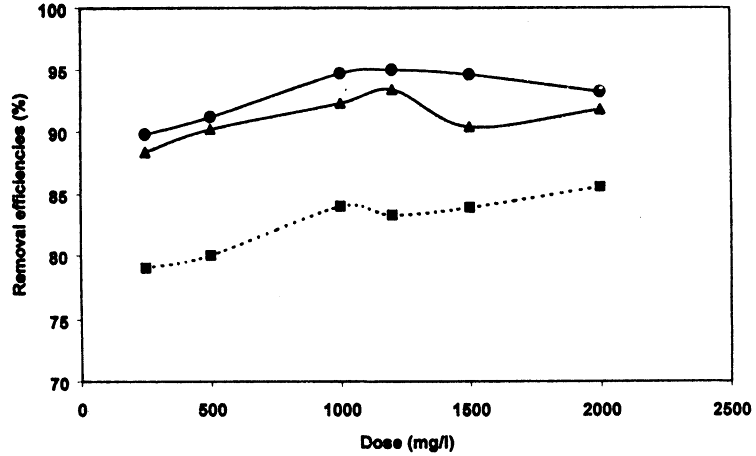

Fig. 3. TSS removal from the wastewater by waterworks sludge (■), ferric chloride (▲) and alum (●).

very effective in terms of TSS removal. Although TSS removal rates did not exceed 87% even for a dose of 2000 mg/L, however, efficiencies were comparable to those obtained with other coagulants. All the coagulants including waterworks sludge achieved more than 80% TSS removal except that the lowest dose of waterworks sludge (250 mg/L) achieved 79% TSS removal. The results were also comparable to results reported by various workers[2, 16, 18].

The results show that typical values were obtained with waterworks sludge. That is, low COD removal and high TSS removal achieved by all coagulants including waterworks sludge. As can be seen from Fig. 2, the COD removal rates varied between 31 and 43%. It was 32% for the lowest sludge dose (250 mg/L) and the highest removal rate was 43% achieved with 1500 mg/L coagulant dose. This, in fact, indicates that there was only about 10% difference between lowest dose (250 mg/L) and highest dose of waterworks sludge (2000 mg/L). The removal rates of TSS varied between 79–87% for all doses of waterworks sludge (Fig. 3.) From these results, low sludge doses (250–500 mg/L) would be recommended because increasing coagulant dose did not affect removal rates dramatically. These coagulant doses are equivalent to 54.8–109.6 mg Fe/L. Taken overall, it can be said that waste waterworks sludge has an appreciable potential for treating wastewater from corrugated papermills.

Kabdasli *et al.*[16] have also reported the use of the coagulants for the treatment of papermill wastewater. They used papermill wastewater which was similar to that used in this study and performed jar test experiment with various coagulants. According to their results, COD removal rates were between 20–30% and TSS removal rates were above 85%. Their results were also comparable with those obtained with waterworks sludge.

In addition to these coagulants, various combinations of waterworks sludge with constant fresh ferric chloride were also examined. For this purpose a constant dose of fresh ferric chloride dose (100 mg/L) with varying waterworks sludge doses (250–2000 mg/L) were used. A settlement period of 30 min was also applied for this set of experiments. Fig. 4 shows a comparison of the effect of addition of fresh ferric chloride on COD removal. As can be seen from Fig. 4, addition of fresh chloride provided about 15% increase for the lowest dose of waterworks sludge. However, for the higher sludge doses there wern't any significant differences between sludge + fresh ferric chloride and fresh ferric chloride alone. In fact, even under the condition of 100 mg/L fresh ferric chloride with 2000 mg/L sludge dose, COD removal rates did not exceed 45%. For TSS removal, similar trend was also observed. Initially addition of fresh ferric chloride provided about 10% increase compared to sludge alone in terms of TSS removal (Fig. 5). For the constant ferric chloride and varying sludge application, slight deterioration was also observed over higher concentrations. However, a combination of 250 mg/L sludge plus 100 mg/L fresh ferric chloride provided the best result in term of TSS removal. This removal efficiency was comparable at doses over 1000 mg/L. These results indicate that the use of low waterworks sludge with fresh ferric chloride (100 mg/L) may provide significant savings of fresh ferric chloride. This in turn means less chemical usage, sludge production and also less cost.

When ferric chloride is added to the water, Fe^{3+} ions are hydrolyzed in water containing alkalinity and insoluble ferric hydroxide is produced over a pH range

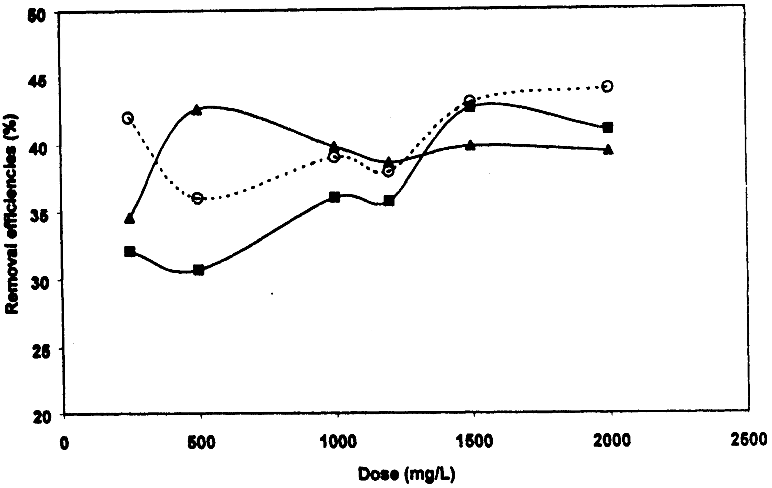

Fig. 4. A comparison of the effect of addition of fresh ferric chloride on COD removal from the wastewater by waterworks sludge (■), ferric chloride (▲) and constant fresh ferric chloride (100 mg/L) + waterworks sludge (O).

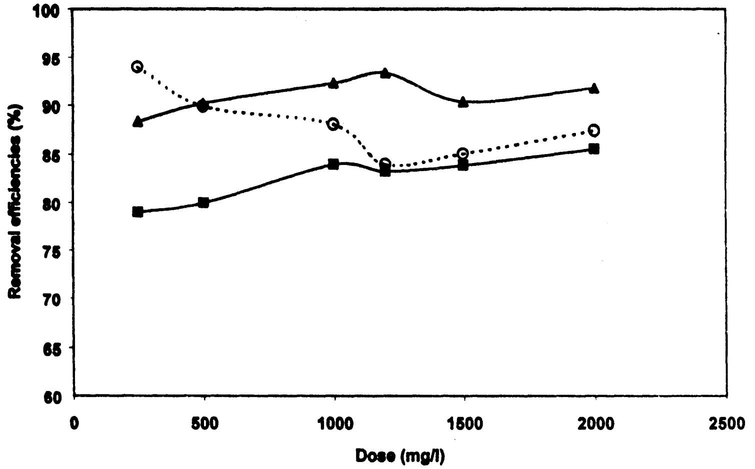

Fig. 5. A comparison of the effect of addition of fresh ferric chloride on TSS removal from the wastewater by waterworks sludge (■), ferric chloride (▲) and constant fresh ferric chloride (100 mg/L) + waterworks sludge (O).

of 3.0 to 13.0. Its reactions are shown in Table-5. The net overall precipitation reaction is

$$2FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ + 3Cl^-$$

During the coagulation process, in the presence of both colloidal matter and Fe^{3+} ions, Fe^{3+} ions act as counter ions to compress the electric double layer around the colloidal matter to promote coagulation. In addition to this, there are two other mechanisms. These are enmeshment by the hydroxy-metal precipitate formed by the ferric chloride and intraparticle bridging or acting as bonding agent between colloidal matters[19]. Colloids may serve as condensation nuclei for these precipitates or may become enmeshed as the precipitates settle. Removal of colloids in this manner is frequently referred to as "sweep-floc" coagulation and this type of coagulation does not depend on neutralisation of surface charge[20]. Conditions for optimum coagulation for this mechanism do not correspond to a minimum zeta potential. However, an optimum pH does exist for each coagulant, depending on its solubility-pH relationship[20]. In this current work waterworks sludge apparently served as a source of condensation nuclei and the addition of fresh ferric chloride optimised the coagulation process due to the formation of hydroxylated species of the ferric chloride. Suspended solids (solid in liquid dispersion) in wastewater from papermill is a colloidal dispersion. Therefore, colloidal matters (suspended solids) in wastewater were enmeshed with the waterworks sludge by sweep floc mechanisms during slow mixing and settling stage. Various researchers have already reported the use of waterworks sludge and the effect of the colloidal matter on coagulation in this manner. Parsons and Daniels[8] have reported that better performance was obtained with unfiltered recovered coagulant than the filtered one. It was suggested that this was due to the impurities present in recovered coagulants acting as points of nucleation, aiding the coagulation process. Chu[12] has also reported that during lead removal through coagulation process using recycled alum sludge and fresh alum, the sweep floc (or enmeshment) mechanism was apparently responsible for the lead removal.

TABLE-5

HYDROLYSIS AND COMPLEX FORMATION EQUILIBRIUMS OF IRON

(Casey[19])

Reaction	log of equilibrium constant (25°C)
$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+$	–2.16
$Fe^{3+} + 2H_2O \rightleftharpoons Fe(OH)_2^+ + 2H^+$	–6.74
$Fe^{3+} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+$	–38
$Fe^{3+} + 4H_2O \rightleftharpoons Fe(OH)_4^- + 4H^+$	–23
$2Fe^{3+} + 2H_2O \rightleftharpoons Fe_2(OH)_2^{4+} + 2H^+$	–2.85

Therefore, ferric chloride based waterworks sludge can be used for the treatment of wastewaters from papermill industry. In order to obtain better results, slight addition of fresh ferric chloride may optimise the removal effect of the ferric sludge. This, in turn, means significant savings from the coagulant usage for the treatment of papermill industry wastewater.

Conclusion

From the work presented here the following conclusions can be drawn:

1. Waterworks sludge will act as a coagulant for papermill industry wastewater for the removal of COD and TSS. Optimum pH was 6 and optimum dose was 500 mg/L.

2. Low COD removals and high TSS removals were obtained with all coagulants including waterworks sludge. Maximum 43% COD and 87.5% TSS removals were obtained with waterworks sludge.These removal rates were found comparable with those achieved by fresh ferric chloride and alum, which are common coagulants used during chemical treatment of papermill industry wastewater.

Various dose combinations of waterworks sludge with constant fresh ferric chloride dose were also examined and it was found that a combination of 250 mg/L sludge plus 100 mg/L fresh ferric chloride provided the best result in term of TSS removal. However, for the higher doses, addition of constant fresh ferric chloride to various waterworks sludge doses did not bring any significant increase compared to rates obtained by sludge alone and fresh ferric chloride alone.

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