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The Wet Oxidation Treatment of Wastewater from SO_x Removal Facilities

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The wet oxidation of sodium dithionate was carried out at an elevated temperature between 100 and 300 °C. The decomposition of the dithionate solution proceeded rapidly at 150—170 °C and (approximately) a complete decomposition occurred at temperatures greater than 200 °C within 30 min. The removed percentage of the dithionate under a large excess of air was independent of the concentration. The addition of iron(II) sulfate and hydrogen peroxide accelerated the decomposition. Wet oxidation was effective for the disposal of wastewater containing dithionates.

Sulfoxylates, except for sulfate in wastewater arising from wet SO_x removal facilities for exhaust gas, are refractory components for COD (chemical oxygen demand) removal (because of their reducing powers). In particular, dithionates comprise 60—85% of total sulfur compounds but are decomposed by oxidizing agents such as chlorine and ozone to an extent which varies from only several % to 40%, in spite of chemical reducing substances.[1,2] Therefore, it has been proposed to treat them by means of ion-exchange, electro-dialysis, and reverse-osmosis methods as well as coagulation and biological disposals.[3,4] However, problems regarding the great quantities of chemicals used and the waste products remained unsolved in those treatments.[3,4]

On the other hand, wet oxidation that is valid for resistant organic matter at an elevated temperature (150—350 °C) and under a high pressure (3—25 MPa), has been put to practical use as a Zimmerman process in the field of wastewater treatment.[5—12] Wet oxidation is especially effective for the treatment of refractory substances for biological decompositions and is capable of recovering inorganic compounds. Furthermore, it is easy to recover energy on the basis of a heat exchange and there are few problems regarding inorganic salts in comparison with the pyrocombution method.

Lack of investigations regarding materials and corrosion for the facilities, however, retarded the application to a wide range of wastewater treatment.[13] Therefore, there have been several studies[14—17] on wet oxidation with catalysts, in order to enhance the decomposition rate or to reduce temperature and pressure used. Wet oxidation using Fenton's reagent[18,19] for refractory organic compounds and its reaction mechanism[20,21] were reported.

This paper deals with the wet oxidation of sodium dithionate as a model experiment for the wastewater treatment of SO_x removal facilities, including refractory dithionates. For practical use, the additive and temperature effects of Fenton's reagent and the protection of apparatus from corrosion due to by-product sulfuric acid have also been examined.

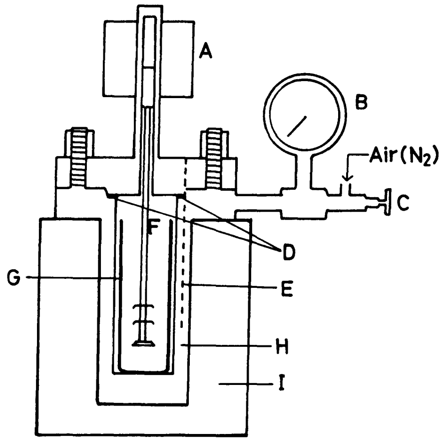

Fig. 1. Apparatus for wet oxidation: A, magnetic coil; B, pressure gauge; C, valve; D, copper packing; E, thermocouples; F, magnet drive rotating axis; G, glass tube; H, reactor; I, electric furnace. The glass tube was used only in Table 6.

Experimental

Apparatus. Wet oxidation and decomposition were carried out in a 200-ml Sakashita SE stainless autoclave equipped with a magnetic stirrer (Fig. 1).

Reagents. Commercial sodium dithionate (Extra Pure) and other chemicals (Guaranteed Reagent) were used without further purification.

Procedures. In the case of wet oxidation, the reaction vessel was charged with a 100-ml aqueous solution of sodium dithionate containing dithionate ion of 3500—35000 mg l^{-1} (or COD_{Mn} of 100—1000 mg l^{-1}) and, subsequently, an initial air pressure of 0.10—8.21 Mpa. Then, the solution was heated to a prescribed temperature between 100 and 300 °C without stirring for 30 min. Finally, the temperature was maintained with stirring for 30 min. Wet decomposition was carried out in the same way as described above, except for an initial nitrogen pressure of 2.13 Mpa. Immediately after the required reaction time, the resulting sulfur dioxide was fixed by connecting three-jointed impingers (sodium hydroxide 1 wt/v % 20 ml×3) during reduced pressure. Sulfuric and sulfurous acids produced in the wet oxidation and decomposition were converted to sodium sulfate and sulfite by pouring an aqueous solution of sodium hydroxide into the autoclave, respectively. They

Table 1. Effect of Temperature on the Wet Oxidation of Sodium Dithionate under an Excess of Air[a)]

Temp	Pressure/MPa		COD_{Mn}[b)]/mg l^{-1}	Removed
°C	t=0[c)]	t=30[c)]	After oxidn.	%
100	2.7	2.8	95.8	0.6
140	2.8	3.5	62.7	35.0
145	3.0	3.6	49.3	48.9
150	3.0	3.9	31.6	67.2
155	3.0	3.9	14.9	84.5
170	3.2	4.0	4.5	95.3
200	3.6	4.4	2.3	97.6
250	4.5	6.2	1.8	98.1
300	6.4	9.1	0.8	99.2

a) Sample of 100 ml containing dithionate ion of 3500 mg l^{-1} was decomposed during promotion time 30 min and reaction time 30 min. The initial pressure of air at 20 °C was 2.13 MPa. b) The COD_{Mn} value for the sample prepared before the oxidation was 96.4 mg l^{-1}. c) The symbols of t=0 and t=30 stand for the reaction at time 0 and 30 min, respectively.

were then subjected to the chemical analyses described below.

Analyses. COD_{Mn} was determined on the basis of the oxygen demand by means of potassium permanganate at 100 °C (JIS K 0102(1981) 17). In the case of coexisting iron(II) ions and/or hydrogen peroxide, the solution was oxidized at room temperature by potassium permanganate; then, the COD_{Mn} was determined as described above. The dithionate concentration was determined from the oxygen demand during the potassium dichromate method (JIS K 0102, 20); its concentration in the presence of sulfite was obtained by subtracting the concentration of sulfite based on the iodine back titration method (JIS K 0102, 40) from the concentration of the both ($S_2O_6^{2-}$+SO_3^{2-}) by the dichromate method. The sulfate concentration was determined by means of the barium chromate method (JIS K 0102, 40-1); in the case of coexisting sulfite, the sulfate concentration was obtained by the subtraction of the sulfite concentration, estimated as described above, from the total concentration of the solution which was oxidized by ozone and then boiled, on the basis of the barium chromate method. The composition of red mud was determined by a fluorescent X-ray analysis of glass beads sintered at 1000 °C within 30 min. The amounts of components involved were: Na_2O, 7.42; K_2O, 0.19; MgO, 0.45; CaO, 1.70; Al_2O_3, 19.97; Fe_2O_3, 28.73; TiO_2, 3.52; SiO_2, 21.97; others, 4.55; Ig loss of carbonate and organic matters, 11.50%.

Results and Discussion

The Wet Oxidation of Sodium Dithionate. Table 1 lists the effect of temperature (100—300 °C) on the wet oxidation of an aqueous solution containing dithionate ions of 3500 mg l^{-1} at an initial air pressure of 2.13 MPa within 30 min. The decomposition of a sodium dithionate solution hardly proceeded at a temperature lower than 100 °C; however, it proceeded rapidly between 150 and 170 °C, at which a dithionate of 95% was removed. An approximately complete decomposition occurred at a temperature higher than 200 °C within 30 min. The change of promotion time, reaching a required reaction temperature, from 15 to 200 min without stirring, scarcely affected the removed percentage of sodium dithionate under stirring conditions.

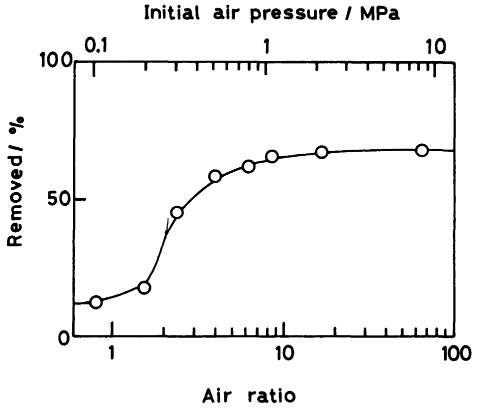

Fig. 2. Correlation of the removed percentage of sodium dithionate with the air ratio or the initial air pressure measured at 20 °C for the wet oxidation of the dithionate at 150 °C under air whose volume was 100 ml. Sample of 100 ml containing dithionate ion of 3500 mg l^{-1} was charged in the reactor.

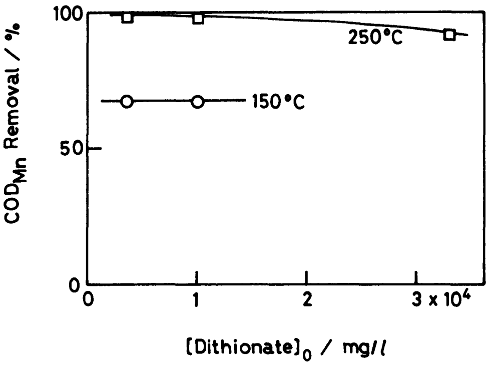

Fig. 3. Correlation of the initial concentration of dithionate with its removed percentage for the wet oxidation of sodium dithionate. The initial pressure of air at 20 °C was 2.1 MPa.

If the wet oxidation of sodium dithionate proceeded according to Eq. 1, the theoretical pressure of air, P MPa, necessary to complete the decomposition of the dithionate ions (A mg) at t °C is approximately given by Eq. 2.

$$2S_2O_6^{2-} + O_2 + 2H_2O \longrightarrow 2SO_4^{2-} + 2H_2SO_4 \qquad (1)$$

$$P = 1.208 \times 10^{-7}\,(273.15+t)A/V \qquad (2)$$

Here, V denotes the volume of air expressed in liters. The air ratio is defined as the ratio of the initial air pressure charged to the theoretical air pressure.

Figure 2 shows the effect of the air ratio on the wet oxidation of sodium dithionate. The removed percentage of dithionate increased remarkably until

Table 2. Effect of Temperature on the Wet Decomposition of Sodium Dithionate under a Nitrogen Atmosphere[a)]

Temp	Pressure/MPa		Dithionate/mg		Sulfite/mg	Sulfate/mg	Total	Removed
°C	t=0[c)]	t=30[c)]	t=0	t=30	t=30	t=30	Sulfate[b)]/mg	%
130	2.8	2.8	339(407)[d)]	333(400)	2.2(2.6)	5.0	408	1.6
140	2.9	3.0	341(409)	326(391)	5.3(6.3)	13.7	411	4.6
150	3.2	3.3	336(403)	308(370)	9.1(10.9)	26.1	407	8.1
180	3.4	3.8	338(406)	150(180)	67(81)	144	405	55.6
200	4.0	4.3	340(408)	43.1(51.7)	114(137)	218	407	87.3
250	5.2	6.0	338(405)	21.3(25.5)	115(138)	242	406	93.7
270	5.7	6.9	342(410)	20.5(24.6)	114(137)	248	410	94.0
300	7.2	8.2	338(405)	6.1(7.3)	120(144)	256	407	98.2

a) Sample of 100 ml containing dithionate of ca. 3400 mg l^{-1} was decomposed during promotion time 30 min and reaction time 30 min. The initial pressure of nitrogen at 20 °C was 2.1 MPa. Various components before and after the reaction are listed in mg in the sample of 100 ml. b) Sum of the resulting sulfate and sulfate equivalent. c) The symbols of t=0 and t=30 represent the reaction at time 0 and 30 min, respectively. d) The amount of sulfate equivalent to that of the corresponding ion is shown in parenthesis.

the air ratio reached ca. 4 and was almost unchanged at an air ratio of more than 10. In general, organic compounds are completely oxidized with a theoretical amount of air under suitable temperatures and pressure conditions. In the wet oxidation of sodium dithionate, however, dissolved oxygen attacks not only the starting dithionate but also the intermediate sulfurous acid to form sulfuric acid. Therefore, the effect of air on the wet oxidation of dithionate became weaker in comparison with that of general organic compounds.

Figure 3 shows a correlation of the dithionate concentration with its removed percentage. In the case of a constant temperature, the removed percentage of the dithionate was independent of its concentration if the air ratio was more than 6. These results are consistent with the fact that the decomposition rate of dithionic acid was proportional to its concentration.[22—27] When the initial concentration of the dithionate was 33000 mg l^{-1}, the decreased removed percentage could be ascribed to a low air ratio of 1.8, as is clear from Fig. 2.

The Wet Decomposition of Sodium Dithionate. In order to clarify the action of oxygen, the wet decomposition of sodium dithionate was examined under an inert gas: in this case, a nitrogen atmosphere. Table 2 lists the respective components before and after the wet decomposition of the dithionate aqueous solution containing dithionate ion of 3400 mg l^{-1} under a nitrogen atmosphere. Since the sum of the respective components calculated in the sulfate equivalent after the reaction was almost equal to the amount of dithionate in the sulfate equivalent before the reaction, the decomposition of the dithionate solution under a nitrogen atmosphere is

$$S_2O_6^{2-} + H_2O \longrightarrow SO_4^{2-} + H_2SO_3. \qquad (3)$$

The removed percentage of dithionate increased considerably at temperatures higher than 180 °C; its percentage in the wet decomposition under an inert gas was of the same order as that in wet oxidation at a lower temperature (by 30—50 °C).

The Mechanism of the Wet Oxidation of Sodium Dithionate. In the case of a neutral aqueous solution, the first step consists of a decomposition of dithionate into sulfate and sulfur dioxide.[22] The resulting sulfur dioxide in an aqueous solution is in equilibrium with the sulfurous acid. When an excess of air is present, sulfurous acid is oxidized to sulfuric acid. Therefore,

$$SO_2 + H_2O + 1/2O_2 = H_2SO_4. \qquad (4)$$

The overall reaction is expressed by

$$S_2O_6^{2-} \xrightarrow{k_1} SO_4^{2-} + SO_2 \xrightarrow[+H_2O,\ O_2]{k_2} SO_4^{2-} + H_2SO_4, \qquad (5)$$

where k_1 and k_2 are the rate constants.

The decomposition rate of dithionic acid into sulfuric and sulfurous acids in the presence of hydrochloric or perchloric acid was proportional to the concentrations of dithionic acid and of the hydrogen ion.[22—26] The activation energy estimated from the decomposition rate in the presence of hydrochloric acid was reported to be 29.8 kcal mol^{-1} (1 cal=4.184 J); similarly, in an alkaline solution the activation energy was evaluated to be 25 kcal mol^{-1}.[25]

From Arrhenius plots between the rate constants calculated on the basis of the first-order reaction of the dithionate concentration, i.e., $k_1 \ll k_2$ in Eq. 5, and the absolute temperature, the activation energy of the decomposition over the range 100—155 °C (Table 1) was evaluated to be 32.5 kcal mol^{-1}.[28] The decomposition percentage at a temperature of 170 °C or greater was lower than that estimated from the activation energy. Although the magnitude of the evaluated activation energy was the same as that for the decomposition of dithionic acid,[25] an extreme assumption may be insufficient for our system, probably because an accumulation of the resulting sulfuric acid accelerates the decomposition of the dithionate. The pH for an aqueous solution contain-

Table 3. Effect of Catalyst Concentration on the Wet Oxidation of Sodium Dithionate at 150 °C[a)]

$[S_2O_6^{2-}]_0$	$[H_2O_2]_0$/COD-O	$[FeSO_4]_0/[H_2O_2]_0$	Removed/%
mg l^{-1}	oxygen ratio	molar ratio	estimated by COD$_{Mn}$
3500	None	None	67.2
3500	0.5	0.2	67.2
3500	1.0	0.2	73.6
3500	1.5	0.2	59.5
3500	2.0	0.2	56.4
3500	1.0	1.0	95.6
3500	1.0	0.3	74.8
3500	1.0	0.1	66.6
10000	None	None	67.1
10000	1.0	None	84.0
10000	None	0.2	96.5
10000	1.0	0.2	95.6

a) Sample volume, promotion time, reaction time, and the initial pressure of air are the same values as described in Table 1.

Table 4. Effect of Temperature on the Wet Oxidation of Sodium Dithionate in the Presence of Fenton's Reagent[a)]

Temp	Pressure/MPa		pH		COD$_{Mn}$/mg l^{-1}		Removed
°C	t=0[b)]	t=30[b)]	Before oxidn.	After oxidn.	Before oxidn.	After oxidn.	%
100	2.7	2.9	2.5	2.2	112	102	8.8
120	2.8	3.0	2.5	1.7	114	62.0	45.6
135	3.0	3.1	2.5	1.6	108	30.9	71.2
150	3.1	3.2	2.5	1.4	103	4.5	95.6
180	3.4	3.7	2.5	1.4	114	1.3	98.9

a) Sample of 100 ml containing dithionate ion of ca. 3500 mg l^{-1} was decomposed during promotion time 30 min and reaction time 30 min. The initial pressure of air at 20 °C was 2.1 MPa; $[H_2O_2]_0$/COD-O oxygen ratio=1.0, $[FeSO_4]_0/[H_2O_2]_0$ molar ratio=1.0. b) The symbols of t=0 and t=30 indicate the reaction at 0 and 30 min, respectively.

ing dithionate ions (3500 mg l^{-1} at 20 °C) varied from 5.8 (before decomposition) to 1.5 (after complete decomposition). The fact that the decomposition percentage of the dithionate increased with an increasing air ratio can be ascribed to the increased concentration of the resulting hydrogen ions.

Since the accumulating sulfuric acid in a wet oxidation is a stronger acid than the sulfurous acid produced in a wet decomposition, it is reasonable from a comparison of the hydrogen ion concentration that the decomposition rate of the dithionate at the same temperature was higher in the former than in the latter. In other words, the wet oxidation of sodium dithionate under an excess of air proceeds at a lower temperature than does wet decomposition under a nitrogen atmosphere.

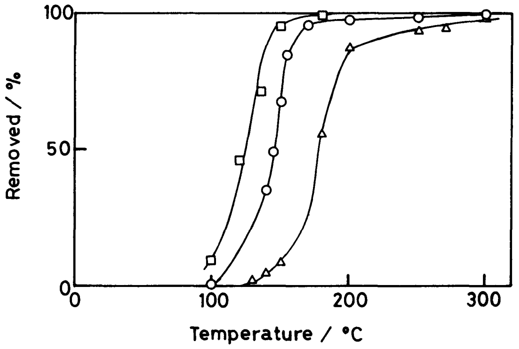

Fig. 4. Effect of temperature on the removed percentage of sodium dithionate for the wet oxidation and decomposition: □, in the presence of Fenton's reagent; ○, under air; △, under nitrogen atmosphere.

The Wet Catalytic Oxidation of Sodium Dithionate Using Fenton's Reagent. Fenton's reagent has a strong oxidation power on the basis of an electron acceptor of the hydroxyl radical produced from hydrogen peroxide in the presence of iron(II) salts. The resulting iron(III) ions are reduced to the starting iron(II) ions by use of hydrogen peroxide and/or a reducing radical produced during the oxidation-reduction process. Most transition metals can be applied as redox catalysts because of their valence transformation abilities. However, it is only the iron(II) ions among the transition metals that do not cause problems during an after treatment.

Table 3 lists the additive effect of catalysts such as hydrogen peroxide and iron(II) sulfate on the removed percentage of the dithionate. The addition of both hydrogen peroxide and iron(II) sulfate brought about a considerably higher decomposition of the dithionate than that in the absence of the additives at the same temperature. The optimum molar ratio of $[FeSO_4]_0$/

Table 5. Additive Effect of Neutralizer on the Wet Oxidation of Sodium Dithionate at 200 °C[a)]

Neutralizer	Additive ratio[b)]	Pressure/MPa		pH[d)]	COD_{Mn}/mg l^{-1}		Removed
		t=0[c)]	t=30[c)]	After oxidn.	Before oxidn.	After oxidn.	%
$CaCO_3$	0.5	3.1	3.8	8.2	303	227	25.1
Red mud (Fe_2O_3)	0.5	3.2	4.0	8.1	305	220	27.8
Red mud (Fe_2O_3)	0.25	3.1	3.6	8.0	305	204	33.1
Red mud (Fe_2O_3)	0.05	3.1	3.6	1.5	303	7.9	97.4

a) Run conditions except for dithionate of ca. 10000 mg l^{-1} are the same as shown in Table 1. b) Molar ratio of neutralizer to the theoretical amount of sulfuric acid produced by complete decomposition. c) t=0 and t=30 indicate the reaction at time 0 and 30 min, respectively. d) The pH value before oxidation was 5.5.

Table 6. The Wet Oxidation of Sodium Dithionate in a Glass Tube[a)]

Run No.	Sample ml	Air ratio	Temp °C	Gap[b)]	COD_{Mn}/mg l^{-1}		Removed %
					Before oxidn.	After oxidn.	
1	100	15.9	150	None	100	33.0	67.0
2	80	13.0	150	Air	108	87.2	19.3
3	80	15.7	150	Air	108	81.3	24.7
4	80	9.1	150	Water	108	71.7	33.6
5	80	15.8	150	Water	108	69.4	35.7
6	50	15.3	160	Air	104	36.6	64.8
7	50	15.8	160	Water	108	24.1	77.7
8	50	15.8	180	Water	108	5.1	95.3

a) Sample containing dithionate ion of ca. 3500 mg l^{-1} was decomposed during promotion time 30 min and reaction time 30 min. Run 1 and the other Runs were carried out without and with a glass tube, respectively. b) Between the glass tube and the high pressure vessel shown in Fig. 1.

$[H_2O_2]_0$ was 1.0 for this system although its value was reported to be 0.2 for the decomposition of organic compounds.[20)]

The temperature effect on decomposition was examined under the optimum conditions (Table 4). Figure 4 shows the temperature dependence of the removed percentages on the wet catalytic oxidation using Fenton's reagent, on the wet oxidation under air, and on the wet decomposition under a nitrogen atmosphere. Figure 4 suggests that the decomposition of the dithionate using Fenton's reagent proceeded at a lower temperature (by ca. 20 °C) compared to that of the wet oxidation without a catalyst.

Treatment of By-Product Sulfuric Acid. The wet oxidation of sodium dithionate resulted in equimolecular amounts of sulfuric acid and sodium sulfate. In the case of the complete decomposition of the aqueous solution containing dithionate ions (3500 mg l^{-1}), the concentration of the resulting sulfuric acid became 0.022 mol l^{-1}. In order to neutralize the acid, the additive effect of bases (such as calcium carbonate and red mud) on the wet oxidation of the dithionate was investigated (Table 5). When a solution after a reaction was weakly basic (pH 8.0—8.2), the decomposition proceeded only by 25.1—33.1%. More acidic conditions for a system after reaction (with the addition of a smaller amount of a base) favor a decomposition.

Protection of Apparatus from Corrosion with a Combined Glass Tube. In the case of purge water drained from S-removal circuit lines for coke-oven gas, titanium containing 0.2% of palladium has been used for the main equipment due to the resulting sulfuric acid and ammonium sulfate.[13)] We examined the wet oxidation using a glass tube in an autoclave (Table 6). The magnitude of the removed percentage of dithionate in a glass tube at 150 °C was less than half of that in an autoclave at the same temperature. However, the former (used at 160 °C) produced almost the same results as the latter at 150 °C. Since the removal difference can be ascribed to a lowering of the thermal conductivity, based on the gap between the glass tube and the high pressure vessel, the removed percentage was improved by filling the gap with water (see in Fig. 1). Corrosion of the autoclave due to the resulting sulfuric acid was not observed during repeated experiments using the glass tube.

Table 7. The Wet Oxidation of Wastewater Involving Dithionate at 180 °C[a)]

Water	pH	COD_{Mn}/mg l^{-1}	Removed/%
Wastewater	5.4	475	
Treated water	0.2	15	96.8

a) The initial pressure of air at 20 °C=2.1 MPa, reaction time=60 min.

The Wet Oxidation Treatment of Wastewater from SO_x Removal Facilities. In light of the above investigations, the wet oxidation of actual wastewater was examined. As Table 7 shows, an almost complete decomposition (97%) occurred. The COD_{Mn} value (475 mg l^{-1}) of the wastewater suggests that the concentration of the dithionate ion was ca. 16600 mg l^{-1}.[29)]

A higher temperature enhances the decomposition percentage and makes it possible to obtain a treated-water $\mathrm{COD_{Mn}}$ of less than 10 $\mathrm{mg\,l^{-1}}$.

Conclusions

The wet oxidation of sodium dithionate, as a model of wastewater involving dithionates from SO_x removal facilities, is summarized as follows.

1. The wet oxidation of an aqueous dithionate solution depends remarkably on the temperature. The wet oxidation did not proceed at a temperature lower than 100 °C, even after long time. However, it rapidly proceeded at 150—170 °C. Approximately a complete decomposition was observed at temperatures higher than 200 °C.
2. The promotion time (15—120 min) reaching a required temperature did not affect the removed percentage of the dithionate unless the solution was stirred during the time.
3. The decomposition percentage of the dithionate under a large excess of air was independent of its concentration.
4. Wet decomposition of the dithionate under a nitrogen atmosphere produced sulfurous acid and wet oxidation under an excess of air produced sulfuric acid. The latter oxidation proceeded at a lower temperature than the former decomposition because of the accelerating effect of the resulting hydrogen ions.
5. Sodium dithionate in aqueous solution was easily decomposed at lower temperatures by using Fenton's reagent. The optimum molar ratio of iron(II) sulfate to hydrogen peroxide was 1.0.
6. The neutralization of the by-product sulfuric acid by using a solid base, resulted in the lowering of the decomposition percentage. A combined glass tube was useful in protecting the reaction vessel from corrosion due to sulfuric acid.
7. In the wet oxidation of actual wastewater at 180 °C, a decomposition percentage of 97% was obtained. It is possible to obtain a treated-water $\mathrm{COD_{Mn}}$ of less than 10 $\mathrm{mg\,l^{-1}}$.

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29) From the correlation of the concentration of dithionate with its $\mathrm{COD_{Mn}}$ value, the following equation was obtained (correlation coefficient r=0.9973; the oxidation of dithionate, 29.07%): $S_2O_6^{2-}$ ($\mathrm{mg\,l^{-1}}$)$=-5.3+35.0\times\mathrm{COD_{Mn}}$ ($\mathrm{mg\,l^{-1}}$).