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Surface Treatment and Facilitated Cleaning of Stainless Steel by Ozonized Air

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Surface treatment of stainless steel by ozonized air was investigated over the range of 0.01 to 0.2% (v/v) ozone (O₃), using nonporous stainless steel particles. Ozonized air contained nitrogen oxides (NO_x) at a NO_x/O₃ ratio of approximately 0.04. When stainless steel particles were treated with ozonized air, nitric acid was formed on their surfaces depending on the O₃ concentration. As a result of ozonized air treatment, the adsorption affinity of water vapor for stainless steel particles decreased and the absolute values of the apparent surface charge density (σ_{app}) of stainless steel particles decreased over the pH range of 3 to 10, resulting in the lower adsorption affinity of bovine serum albumin (BSA). The σ_{app} curves of stainless steel particles treated with ozonized air at 0.15 to 0.2% O₃ were very similar to the curves of the particles treated with 10 and 30% HNO₃. These results indicated that nitric acid formed during ozonized air treatment brought about the modification of the surface charge of stainless steel particles. Ozonized air pretreatment of stainless steel particles fouled with BSA or calcium hydrogenphosphate markedly facilitated their removal during subsequent alkali cleaning or rinsing through O₃ oxidation or descaling with nitric acid.

Key words : Facilitated cleaning/Stainless steel/Ozonized air/Nitric acid/Surface treatment.

INTRODUCTION

In the food industry, products are often contaminated chemically and microbiologically from equipment surfaces during storage, transport, and processing. Cleanliness of product-contact surfaces is a very important issue in preventing contamination of the product processed. Food residues on product-contact surfaces that serve as nutrients for microorganisms should be removed by routine cleaning after each set of processing operations. In general, food residues on heated surfaces, e.g., milk deposits, consist of alkali-soluble (organic) and acid-soluble (inorganic) components (Burton, 1968; Lalande et al., 1984), and they are commonly removed by applying both alkaline and acidic detergents (Dunsmore et al., 1981; Jeurnink and Brinkman, 1994). Caustic solution is very

effective and is widely used to clean equipment because of its excellent ability to solubilize a variety of organic substances. Alkaline detergent is composed mainly of sodium hydroxide, to which chlorinated compounds, phosphates, chelating agents, and surfactants are added in order to enhance the cleaning efficiency (Clegg, 1962; Graßhoff, 1988; Twomey, 1968). On the other hand, nitric acid, phosphoric acid, and organic acids are used for acid cleaning to dissolve mineral deposits. However, acidic solutions except for nitric acid and chlorine solution cause some corrosion to stainless steel, the material most widely used in the construction of food-processing equipment. Roughening the inner surface of stainless steel causes reduction of the cleaning efficiency (Timperley, 1981). In addition, the use of large quantities of detergent is fairly costly, and yields a high waste load for biological wastewater treatment.

Recently, ozone (O₃) has been increasingly used as an alternative oxidizing agent to chlorine. Ozone

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has a strong sterilizing ability and has been used successfully in drinking water treatment as a substitute for chlorine (Rice et al., 1981; Singer, 1990; Smith and Moss, 1993). Ozone is produced commercially from either oxygen or air by a silent surface discharge ozonizer. Ozonized oxygen generated from an oxygen-fed ozonizer consists only of oxygen species (O_2 , O_3 , and O) and it reacts with fouling deposits directly as molecular O_3 or indirectly as ozone-derived free radicals. Our recent studies demonstrated that pretreatment with ozonized oxygen to aluminum oxide (Al_2O_3) fouled with bovine serum albumin (BSA) markedly accelerated the removal of BSA during subsequent alkali cleaning through partial decomposition of the adsorbed BSA (Takehara et al., 2000; Urano and Fukuzaki, 2001). On the other hand, silent discharge in an air-fed ozonizer produces not only O_3 but also small amounts of nitrogen oxides (NO_x) such as NO , NO_2 , NO_3 , N_2O , and N_2O_5 (Braun et al., 1990; Kogelschatz and Baessler, 1987; Yagi and Tanaka, 1979). Among NO_x components, dinitrogen pentoxide (N_2O_5) is further transformed into nitric acid (HNO_3) through reaction with traces of H_2O (Kogelschatz and Baessler, 1987). This suggests that treatment of solid surfaces including stainless steel by ozonized air, which contains both O_3 and NO_x , under atmospheric conditions would result in the formation of nitric acid on their surfaces. Nitric acid has so far been used for chemical passivation of stainless steel (Asami and Hashimoto, 1979) and for descaling (Twomey, 1968).

In the present study, the effectiveness of treatment of clean and fouled stainless steel with ozonized air was investigated and compared with that of treatments with ozonized oxygen and HNO_3 . We used nonporous stainless steel particles as a model material, and BSA and calcium hydrogenphosphate ($CaHPO_4$) as model fouling deposits. This paper describes how ozonized air treatment could modify the surface charge of stainless steel and facilitate cleaning of BSA-fouled and $CaHPO_4$ -fouled stainless steel owing to the action of O_3 and nitric acid.

MATERIALS AND METHODS

Materials and chemicals

Nonporous stainless steel particles (SUS 316 L), BSA (Fraction V), and other chemicals (analytical grade) were the same as those described previously (Fukuzaki et al., 2001).

Surface treatments of stainless steel particles

Ozonized air was generated from dry air by a silent discharge ozonizer (Model 961; OHNIT Co. Ltd., Okayama) equipped with an ozone monitor (PG-320; Ebara Jitsugyo Co. Ltd., Tokyo). A 10-g aliquot of

untreated stainless steel particles was placed in a cylindrical glass column (28mm diameter \times 220mm length) which was connected to the ozonizer device. Ozonized air (0.01 to 0.2% v/v, O_3) was passed through the glass column at a flow rate of 5 l/min for 60min at room temperature. Relative humidity in the glass column was not controlled. After the treatment, each 2-g aliquot portion of the ozonized air-treated stainless steel particles was transferred into a 25-ml glass vial, and then rinsed three times with 10ml of deionized water (40 °C, 140 oscillations per min, 10min) by centrifugation ($2300 \times g$ for 1min). After being rinsed, the ozone-treated stainless steel particles were dried at 150 °C. Specific surface areas of ozonized air-treated stainless steel particles varied slightly between 0.40 (non-treated) and 0.50 m^2/g , depending on ozone concentrations. As a comparison, treatment of stainless steel particles with ozonized oxygen, generated from pure oxygen (99.999% v/v), was also conducted at O_3 concentration of 0.2% under the same conditions as those for ozonized air treatment.

Stainless steel particles were also treated with HNO_3 solutions to compare the effects of nitric acid formed from the ozonized air treatment and HNO_3 solution on the surface properties of stainless steel. Twenty-gram aliquots of non-treated stainless steel particles were put into 300-ml flasks containing 200ml of 10% and 30% HNO_3 and treated for 1 h at 60 °C. After HNO_3 treatments, HNO_3 solutions were carefully decanted, and the particles were suspended in 200ml of deionized water. The suspensions were then transferred into 500-ml centrifugation tubes and rinsed 10 times each with 300ml of deionized water by centrifugation ($1700 \times g$ for 5min). After being rinsed, the particles were dried at 150 °C. Specific surface areas of the particles treated with 10% and 30% HNO_3 were 0.49, and 0.59 m^2/g , respectively.

In all surface treatments, three replicate samples were prepared per concentration of O_3 and HNO_3 .

X-ray photoelectron spectroscopic (XPS) analysis

The chemical composition of the outermost surfaces of stainless steel particles was determined by XPS analysis. XPS analysis was performed on JPS-90MX MICRO spectrometer (JEOL Ltd., Tokyo) using a MgK_{α} (1253.6 eV) X-ray source (10kV and 20mA). The residual pressure in the spectrometer during data acquisition was always lower than 5×10^{-7} Pa. For the analysis, stainless steel particles were molded into a plate (13mm diameter \times 1mm thickness) by compression (40 MPa, 2min). The pellet obtained was then transferred into the high vacuum chamber of the XPS instruments and allowed to stand for 24h. No argon ion etching was performed. The measured spectra

were Fe 2p_{3/2}, Cr 2p_{3/2}, Ni 2p_{3/2}, O 1s, and C 1s, and the quantification of the elements was based on the area intensity and atomic percentage. To compensate for sample charging during the analysis all the binding energies were referred to the C 1s signal at 284.7 eV.

Water vapor adsorption and surface charge measurements

Measurement of the isotherm of water vapor adsorption onto stainless steel surfaces (25°C) and BET analysis of the isotherm were carried out as described previously (Fukuzaki et al., 2001). The apparent surface charge density (σ_{app}) and apparent point of zero charge (pzc_{app}) of stainless steel particles were determined by potentiometric titration as described previously (Fukuzaki et al., 2001). The measurements of the water adsorption isotherms and the σ_{app} curves were carried out for each of the three replicate samples per treatment.

Fouling experiments

Adsorption of BSA on stainless steel particles (40°C) and determination of the amount of BSA adsorbed (Γ_{BSA}) were carried out as described previously (Fukuzaki, et al., 2001). To determine the effect of surface treatment of stainless steel particles on Γ_{BSA} , each adsorption experiment was replicated three times for each of the surface-treated particles.

The CaHPO₄-fouled stainless steel particles were prepared at 25°C as follows. A 2-g aliquot of untreated stainless steel particles was put into a 100-ml flask containing 50ml of CaHPO₄ solution (5.6mM, pH4.0). By adding 4.5ml of 0.1M KOH into the suspension, CaHPO₄ precipitate was deposited on stainless steel particles with agitation at 200rpm for 10min. After agitation, the CaHPO₄-fouled particles were collected by centrifugation (2300 × *g*, 1min), and the collected particles were washed twice with 50ml of deionized water, also by centrifugation (2300 × *g*, 1min). The amount of deposited CaHPO₄ (Γ_{CaHPO_4}) was calculated from the amount of Ca removed after treatment with 0.1M HNO₃ at 40°C for 2h.

Cleaning experiments

To determine the effect of ozone pretreatment on cleaning, 4.0g of BSA-fouled particles (Γ_{BSA} = ca. 2.0 mg/m²) and 0.5g of CaHPO₄-fouled particles (Γ_{CaHPO_4} = ca. 66mg/m²) were pretreated with ozonized air or ozonized oxygen at 0.2% (v/v) O₃ for 30min, respectively.

The time course of BSA desorption from stainless steel surfaces was determined during repeated-batch cleaning at 40°C as described previously (Fukuzaki et al., 2001). A 4.0-g aliquot of BSA-fouled stainless

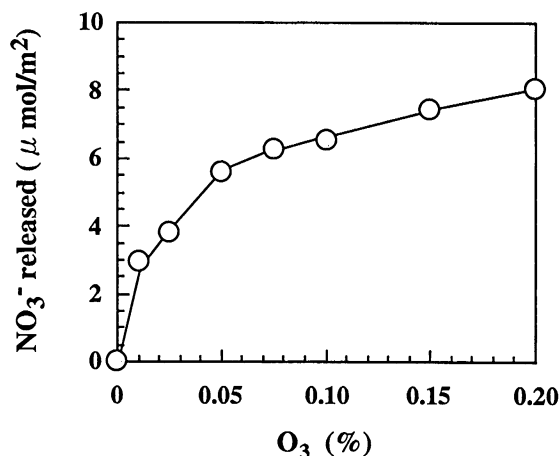


FIG. 1. Concentration of nitrate ions released from ozonized air-treated stainless steel particles during rinsing. A 2-g aliquot of ozonized air-treated stainless steel particles was rinsed with 10ml of deionized water (25°C) in a 25-ml glass vial with shaking (140 oscillations per min) for 10min.

steel particles was cleaned using 10ml of deionized water (pH5.7) for 50min followed by the use of 0.01M NaOH for 180min. The headspace of the vial was replaced by N₂ gas throughout cleaning experiment. The BSA desorption curve was obtained by plotting the logarithm of the amount of BSA remaining at time *t* (*S*) relative to that immediately before alkali cleaning (*S*₀ = Γ_{BSA}), $\ln S/S_0$, against cumulative cleaning time.

Cleaning of CaHPO₄-fouled stainless steel particles was also conducted in a batchwise manner by introducing 0.5g of CaHPO₄-fouled particles and 10ml of deionized water or 0.1M HNO₃ in a 25-ml glass vial, which was then reciprocally shaken at 40°C for 2h.

Analytical procedures

Nitrate (NO₃⁻) was analyzed with an ion chromatograph (2010i; DIONEX, Osaka) equipped with an IonPac AS4A-SC column and an electric conductivity detector. The column was operated with 40mM KOH at a flow rate of 1.0ml/min. NO_x in ozonized air was measured by an NO_x analyzer (CLA-510SS, Horiba Ltd., Tokyo) with NO gas as the standard. BSA (non-ozone-treated and ozone-treated) was measured using the Lowry-Folin method as described previously (Urano and Fukuzaki, 2001). The amounts of iron, chromium, nickel, and calcium were measured by using an inductively coupled plasma (ICP) spectrometer as described previously (Fukuzaki et al., 1995).

RESULTS AND DISCUSSION

Formation of nitric acid on stainless steel surfaces

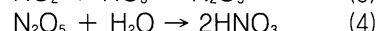
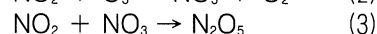
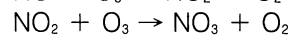
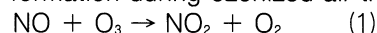
TABLE 1. Atomic composition of the outermost surfaces of stainless steel particles treated with ozonized air, ozonized oxygen, and HNO₃ solutions.

Stainless steel	Component (atom %)			
	Cr	Fe	O	C
Non-treated	3.6	4.2	54.7	23.5
Ozonized air-treated	4.0	3.0	52.8	23.8
Ozonized oxygen-treated	3.3	3.5	51.9	22.7
10% HNO ₃ -treated	8.6	2.2	51.7	22.1
30% HNO ₃ -treated	8.9	1.9	54.2	21.9

Stainless steel particles were treated with ozonized air and ozonized oxygen at 0.2% O₃ for 1h at room temperature. Argon ion etching was not conducted. Another major spectrum was observed at 101.7 eV which assigned to Si 2p.

Stainless steel particles were treated with ozonized air at O₃ concentrations of 0.01 to 0.2% (v/v), in which NO_x species were contained at NO_x/O₃ ratio of approximately 0.04 (data not shown). When all the ozonized air-treated stainless steel particles were rinsed with deionized water, NO₃⁻ was detected in the rinse water. Figure 1 shows concentration of NO₃⁻ released in rinse water as a function of O₃ concentration. NO₃⁻ concentration increased with increasing concentrations of O₃ and hence of NO_x, with a maximum value of approximately 8.0 μmol/m². This suggested that nitric acid was formed on stainless steel surfaces during ozonized air treatment. It has been reported that the NO_x formed in the silent discharge of

an air-fed ozonizer played an important role in the catalytic cycle of O₃ destruction (Yagi and Tanaka, 1979) and that NO_x species were transformed into nitric acid via the formation of N₂O₅ in the presence of O₃ and H₂O (Kogelschatz and Baessler, 1987). According to previous reports (Yagi and Tanaka, 1979; Kogelschatz and Baessler, 1987), the following mechanism is proposed for the predominant pathway of nitric acid formation during ozonized air treatment:



It is conceivable that water molecules physisorbed on stainless steel surfaces were involved in the reaction with N₂O₅.

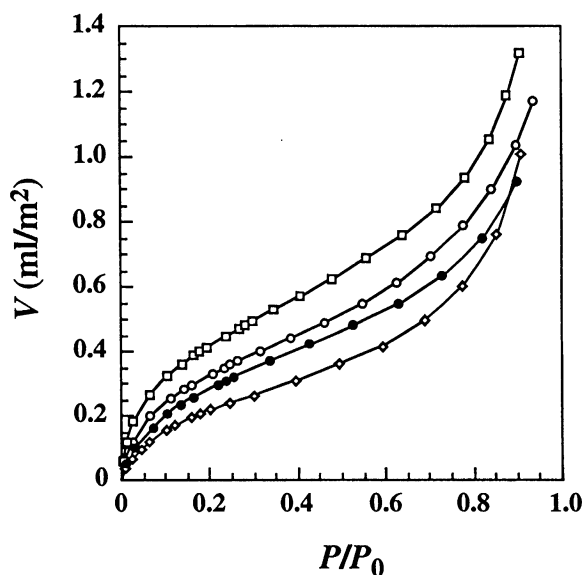


FIG. 2. Isotherms of water vapor adsorption on non-treated, ozonized air-treated, and 30% HNO₃-treated stainless steel particles at 25°C. Stainless steel particles were treated with ozonized air at 0.2% (vol/vol) O₃. Symbols: ○, non-treated particles; □, ozonized air-treated particles before rinsing; ●, ozonized air-treated particles after rinsing; ◇, 30% HNO₃-treated particles.

Characterization of outermost surfaces of ozonized air-treated stainless steel

Table 1 shows the atomic composition of main

TABLE 2. BET equation constants for the adsorption of water vapor onto the stainless steel particles treated with ozonized air, ozonized oxygen, and HNO₃ solutions.

Stainless steel	V _m (ml/m ²)	c (-)
Non-treated	0.32	26.3
Ozonized air-treated		
with rinse	0.26	18.5
without rinse	0.37	28.9
Ozonized oxygen-treated	0.28	24.8
10% HNO ₃ -treated	0.22	18.3
30% HNO ₃ -treated	0.21	16.1

Stainless steel particles were treated with ozonized air and ozonized oxygen at 0.2% O₃ for 1h at room temperature. The constants were derived from linear regression fits of the BET equation to the water vapor adsorption data in the P/P₀ range of 0.05 to 0.30.

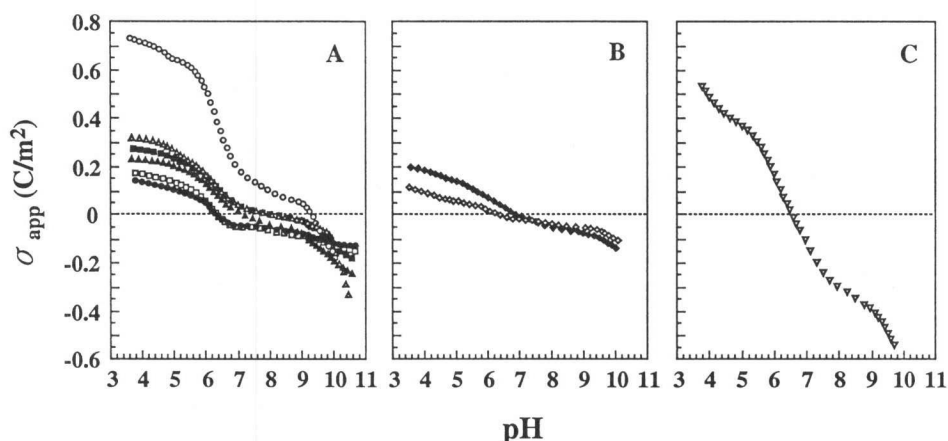


FIG. 3. σ_{app} curves of non-treated, ozonized air treated, HNO_3 -treated, and ozonized oxygen-treated stainless steel particles as a function of pH. Potentiometric titration was conducted in 10^{-3} M KNO_3 solution. Symbols: (A) \circ , non-treated particles; \triangle , ozonized air-treated particles (0.02% O_3); \blacksquare , ozonized air-treated particles (0.05% O_3); \blacktriangle , ozonized air-treated particles (0.1% O_3); \square , ozonized air-treated particles (0.15% O_3); \bullet , ozonized air-treated particles (0.2% O_3); (B) \blacklozenge , 10% HNO_3 -treated particles; \diamond , 30% HNO_3 -treated particles; (C) ∇ , ozonized oxygen-treated particles (0.2% O_3).

metal components of the outermost surfaces of stainless steel particles treated with ozonized air (0.2% O_3), ozonized oxygen (0.2% O_3), and HNO_3 solutions. The ozonized air treatment showed a slight increase in the atomic ratio of chromium to iron in the outermost surfaces, whereas no significant change in the chromium/iron ratio was observed in ozonized oxygen-treated stainless steel. Treatments with 10% and 30% HNO_3 resulted in the significant enrichment of chromium in the surfaces. These results indicated that the nitric acid formed during ozonized air treatment could contribute to a slight increase in chromium content. The 10% and 30% HNO_3 treatments lead to enrichment of chromium throughout the passive film on stainless steel (Asami and Hashimoto, 1979), whereas ozonized air treatment appears to modify only a very thin layer of the passive film on stainless steel. No significant amount of nickel was detected in the outermost surfaces of all the stainless steel.

To assess the variation in the surface hydroxyl groups ($\text{M}-\text{OH}$) on stainless steel particles by surface treatments, isotherms of water vapor adsorption on stainless steel particles were measured. Figure 2 shows the isotherms for water vapor adsorption on non-treated particles, ozonized air-treated particles at 0.2% O_3 before and after rinsing, and 30% HNO_3 -treated particles. The amounts of water vapor adsorbed (V) were plotted against the relative vapor pressure (P/P_0), where P and P_0 are the equilibrium and saturated vapor pressures, respectively. The ozonized air-treated particles without rinsing apparently exhibited a higher affinity for water than the non-treated particles. This is evidently due to the presence of nitric acid that is hygroscopic on the stainless steel surfaces. On the other hand, the isotherm on the rinsed ozonized air-treated particles was

characterized by a lower affinity for water. The 30% HNO_3 -treated particles showed a much lower affinity for water. Table 2 shows the results of BET analysis of the isotherms on the particles obtained by the all surface treatments in the low P/P_0 range of 0.05 to 0.3. The monolayer saturation amounts (V_m) and BET c values, reflecting the adsorption affinity, were considerably lower for the particles treated with 10% and 30% HNO_3 than those for non-treated particles. Ozonized air treatment (with rinsing) also resulted in the relatively lower V_m and BET c values compared with those for ozonized oxygen-treated particles and non-treated particles. These results indicate that nitric acid formed during ozonized air treatment was responsible for a decrease in the number of adsorption sites for water vapor, i.e., hydroxyl groups, on stain-

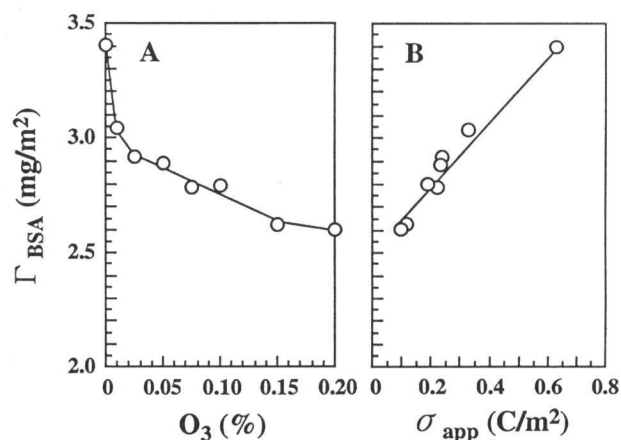


FIG. 4. Γ_{BSA} on ozonized air-treated stainless steel particles at O_3 concentrations of 0.01 to 0.2% (v/v). The adsorption experiment was conducted in a 25-ml glass vial at 40°C and at pH 5.2. (A) Γ_{BSA} as a function of O_3 concentration; (B) Γ_{BSA} as a function of σ_{app} at pH 5.2.

less steel surfaces. In connection with this, Asami and Hashimoto (1979) have reported that treatments of type 304 and 316 stainless steel with 10% and 30% HNO_3 gave smaller ratios of oxygen in M–OH to the total amount of oxygen (oxygen in M–OH plus oxygen in M–O–M) in the surface films, suggesting that the OH-type oxygen in the surface film was transformed into the MOM-type oxygen.

Since the surface charge of oxide and stainless steel is established by the protonation (M–OH_2^+) or deprotonation (M–O^-) of surface hydroxyl groups (Fukuzaki et al., 1998; Parks and Bruym, 1962), varying the degree of surface hydroxylation gives rise to the change in the electrostatic nature of stainless steel particles. Figure 3 shows the representative σ_{app} curves of non-treated, ozonized air-treated, ozonized oxygen-treated, and HNO_3 -treated stainless steel particles as a function of pH. The pzc'_{app} of the non-treated particles was found to be 9.2. The pzc'_{app} of ozonized air-treated particles were situated at points corresponding to more acidic pH values than the pzc'_{app} of the non-treated particles (Fig. 3A). The degrees of the shift in the pzc'_{app} and of decrease in the absolute values of σ_{app} depended on ozone concentration. The absolute values of σ_{app} of 10% and 30% HNO_3 -treated particles were very low over the pH range of 3 to 10, indicating the formation of electrostatically inert surfaces (Fig. 3B). The σ_{app} curves of the ozonized air-treated particles at 0.15 to 0.2% O_3 , giving the

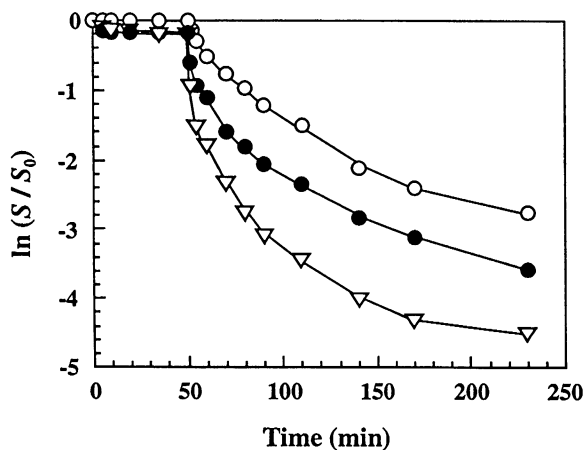


FIG. 5. Time courses of BSA desorption from stainless steel particles during cleaning with 0.01M NaOH with and without ozone pretreatment. The cleaning experiment was conducted in a 25-ml glass vial at 40°C with reciprocal shaking (140 oscillations per min) by a repeated-batch procedure. BSA-fouled stainless steel particles were pretreated with ozonized air or ozonized oxygen at 0.2% (v/v) O_3 for 30min, and cleaned using deionized water for 50min followed by using the NaOH solution for 180min. Symbols: ○, alkali cleaning alone; ●, pretreated with ozonized air; ▽, pretreated with ozonized oxygen.

TABLE 3. Effect of pretreatment with ozonized air on the removal of CaHPO_4 deposited on stainless steel particles.

Cleaning	Ca removed	
	(mg/m ²)	(%)
0.1M HNO_3	19.6	100
H_2O alone	0.4	2.0
H_2O +pretreatment with ozonized air	7.4	37.8
H_2O +pretreatment with ozonized oxygen	0.9	4.6

The CaHPO_4 -fouled stainless steel particles were washed with 0.1M HNO_3 or deionized water with and without pretreatment with ozonized air or ozonized oxygen at 0.2% O_3 for 30min at room temperature.

pzc'_{app} of 6.3, were similar to the curves of 10% and 30% HNO_3 -treated particles. The pzc'_{app} was also lowered to 6.5 by treatment with ozonized oxygen at 0.2% O_3 whereas the absolute values of σ_{app} were relatively higher compared with those from the curves of ozonized air-treated particles at 0.2% O_3 (Fig. 3C). The difference between the σ_{app} curves of the particles treated with ozonized air and ozonized oxygen at 0.2% O_3 could be interpreted as arising from the action of the nitric acid formed during ozonized air treatment.

BSA adsorption on ozonized air-treated stainless steels

To minimize the effects of electrostatic interaction between BSA molecules on their adsorption, BSA adsorption was conducted at the pzc'_{app} of BSA (pH5.2). Figure 4 shows Γ_{BSA} values on ozonized air-treated stainless steel particles. The Γ_{BSA} decreased gradually from 3.4 to 2.6mg/m² with increasing O_3 concentration from 0.01 to 0.2% (Fig. 4A). The Γ_{BSA} values as a function of the σ_{app} of stainless steel particles at pH5.2 are shown in Fig. 4B. An approximate linear correlation between Γ_{BSA} and σ_{app} was observed, which is in good agreement with the results obtained for Γ_{BSA} on the ozonized oxygen-treated stainless steel particles (Fukuzaki et al., 2001). The Γ_{BSA} on the 10% and 30% HNO_3 -treated particles were 2.5 and 2.3mg/m², respectively. Obviously, Γ_{BSA} depends on the σ_{app} of stainless steel particles. On positively charged solid surfaces, BSA is reported to be electrostatically adsorbed via carboxyl groups on the molecule (Fukuzaki et al., 1998; Urano and Fukuzaki, 2000). The decrease in Γ_{BSA} on the ozonized air-treated stainless steel was probably due to the decrease in the number of adsorption sites, i.e., protonated hydroxyl groups, on stainless steel surfaces for carboxyl groups on the BSA molecule.

Effect of pretreatment of fouled stainless steel particles by ozonized air

The effect of pretreatment of BSA-fouled stainless steel particles by ozonized air on the efficiency of alkali cleaning was examined and compared with that of ozonized oxygen pretreatment. Figure 5 shows the desorption curves of BSA during alkali cleaning after pretreatment with ozonized air or ozonized oxygen at 0.2% O₃ for 30min. By pretreatment with ozonized air or ozonized oxygen, small amounts of BSA were desorbed during rinsing and the removal of BSA was accelerated markedly during subsequent alkali cleaning. Probably, the acceleration of alkali cleaning could be attributed to partial decomposition of the BSA molecule into low-molecular fragments by O₃ (Urano and Fukuzaki, 2001). Pretreatment with ozonized oxygen was found to be more effective on BSA removal than that with ozonized air. It is presumed that the nitric acid formed might induce the acid-denaturation of the BSA molecule or diminish the alkalinity of a low-concentration NaOH solution (0.01M) to some extent, thereby causing a slight decrease in the solubility of BSA in the NaOH solution.

Table 3 shows the effect of pretreatment of CaHPO₄-fouled stainless steel particles by ozonized air on their cleanability. The deposited CaHPO₄ was completely removed by cleaning with 0.1M HNO₃. Ozonized air pretreatment resulted in the removal of a large amount of CaHPO₄ only by rinsing with deionized water. This result indicated that nitric acid formed was responsible for the dissolution of the deposited CaHPO₄ into the rinse water. On the other hand, only small amounts of CaHPO₄ were removed both by rinsing alone and by that combined with ozonized oxygen pretreatment. Thus, the effects of pretreatment with ozonized air and ozonized oxygen are different for the organic and inorganic deposits due to the formation of nitric acid.

The results presented in this paper show that ozone (O₃) and small amounts of nitric acid formed during ozonized air treatment could contribute both to the formation of electrostatically inert surfaces and to facilitated removal of protein and mineral deposits on stainless steel.

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