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Original Article

Dental Erosion and Sulfuric Ion Exposure Levels in Individuals Working with Sulfuric Acid in Lead Storage Battery Manufacturing Plant Measured with Mouth-rinse Index

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Abstract

To investigate dental erosion in employees working with sulfuric acid at a lead storage battery manufacturing plant and level of personal exposure to sulfuric ions, we measured sulfuric ion concentrations in the mouth rinse of those employees. We also measured exposure levels from air samples obtained from 2 employees from the same plant who did not work with sulfuric acid using a portable air sampler. At the same time, we collected and compared their mouth rinses with those from other employees. More specifically, we measured and compared sulfuric ion, calcium, and magnesium concentrations, along with pH levels from the mouth rinse of these two groups. Positive correlations were found between sulfuric ion and calcium concentrations ($r=0.61$, $p<0.005$), calcium and magnesium concentrations ($r=0.61$, $p<0.005$), Ca/Mg and calcium concentrations ($r=0.64$, $p<0.005$), and sulfuric ion and magnesium concentrations ($r=0.55$, $p<0.005$). Negative correlations were found between sulfuric ion concentrations and pH levels ($r=-0.31$, $p<0.01$), and magnesium concentrations and pH levels ($r=-0.32$, $p<0.01$). This suggests that mouth rinse from employees working with sulfuric acid could function as an indicator of sulfuric ion concentration in the work environment. Furthermore, this could lead to the development of a more accurate indicator of individual exposure.

Key words: Dental erosion—Occupational health—Battery manufacturing plant—Sulfuric acid—Mouth rinse

Introduction

In recent years, there have been a number of case reports concerning dental erosion[1,2,4,6–8,21–23] in lead storage battery manufacturing plants due to improvements in production and work environment management. However, in a lead storage battery factory where dental erosion had been identified in the past, local sulfuric ion concentration in the work environment was found to be above the maximum permissible concentration (1.0 mg/m^3)[18]. Therefore, in our previous study[18], workers handling sulfuric acid were given an oral examination and rates of dental erosion by tooth type, number of working years and sulfuric acid density in the work environment investigated. Where dental erosion was diagnosed, the degree for each case was identified according to a diagnostic criterion. No development of dental erosion was detected in the maxillary teeth. Erosion was concentrated in the mandibular teeth, especially anteriorly. Prevalence of dental erosion caused by sulfuric acid gases and mists was as high as 20%. Rates of dental erosion rose precipitously after 10 working years. The percentages of workers with dental erosion were 42.9% for 10–14 years, 57.1% for 15–19 years and 66.7% for over 20 years, with 22.5% for total number of workers. The percentage of workers with dental erosion rose in proportion to work environmental sulfuric acid density: 17.9% at 0.5–1.0, 25.0% at 1.0–4.0 and 50.0% at 4.0–8.0 mg/m^3. These results suggested that it was necessary to evaluate not only length of exposure, but also sulfuric ion concentrations in the air.

According to a report by Nishimura *et al.* on dental erosion suffered by workers at a dye manufacturing facility, the amount of urinary calcium excretion of the workers exposed to sulfuric acid was greater than that of those not exposed, and the pH levels of the exposed workers' saliva indicated more acidity than those of the non-exposed workers[13]. It was reported that this had an impact on the amount of urinary calcium excretion from decalcification of the tooth surface due to sulfuric acid[3,9,10,14,19,20]. Suyama reported that cadmium concentrations in the saliva and mouth rinse of employees working with cadmium reflected cadmium concentrations in the work environment[16]. In the field of industrial hygiene, measurement of individual exposure to toxic substances is important[7,16]. Therefore, in order to investigate the onset of dental erosion, we collected mouth rinse from employees to measure each individual's level of exposure to sulfuric ions in the atmosphere[1,16].

In this study, we measured and compared sulfuric ion levels in mouth rinse and air samples obtained from 2 employees who did not work with sulfuric acid and others who did from the same factory. Air samples were obtained by means of portable air samplers. We measured sulfuric acid, calcium, and magnesium concentrations, along with pH levels, and compared these levels with mouth rinse collected from white-collar employees in the plant. The present study focuses on intraoral conditions (dental erosion) and the indoor (labor) environment.

Materials and Methods

1. Subjects

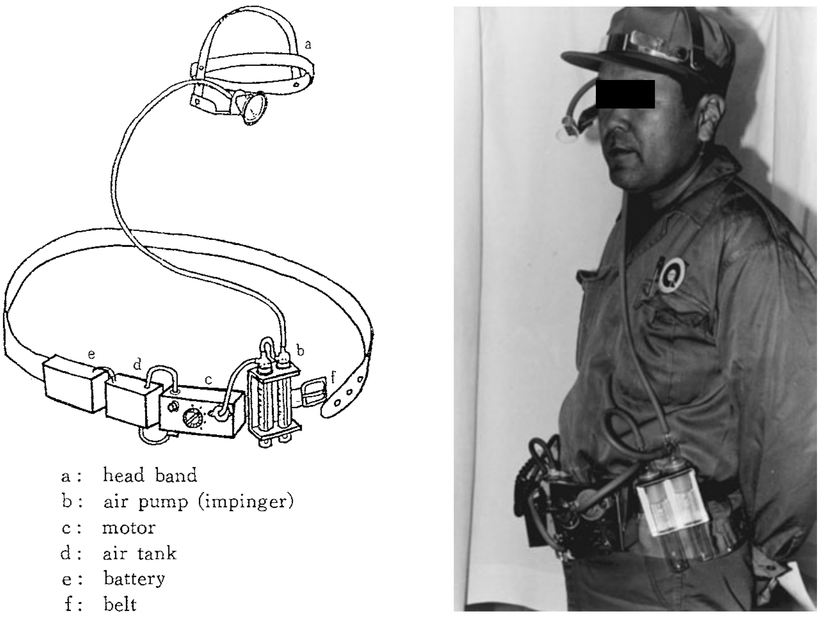
Mouth rinse was collected from 40 employees working with sulfuric acid, 8 employees not working with sulfuric acid (office staff), and 8 controls (volunteers from our institution), making a total of 56 male subjects. In addition, 2 employees not working with sulfuric acid were selected for collection of air samples in addition to mouth rinse samples.

2. Mouth rinse collection

Two hours after lunch, each subject rinsed his mouth once with 30 ml secondary distilled water (pH: 6.89) for 10 sec, then spat it into a 50 ml, wide-mouthed plastic bottle.

3. Measurement of individual levels of exposure

To help measure sulfuric ion concentration in the work environment, mouth rinse was also collected at the end of the working shift



1-1 1-2

Fig. 1 Personal air sampler
1-1: Components of personal air sampler, 1-2: Employee wearing personal air sampler.

from 2 employees who did not work with sulfuric acid (Worker A and Worker B), but were from the same plant, and their sulfuric ion concentrations, calcium, magnesium, and pH levels measured (Figs. 1-1, 1-2). These 2 subjects wore portable air samplers. Secondary distilled water was the collection medium.

4. Measurement of sulfuric acid concentration in the work environment

Sulfuric ion concentration was measured in 13 workplaces in which sulfuric acid was present and in 5 workplaces in which it was not. Portable samplers were used for the measurements and secondary distilled water as the collection medium. Air was absorbed at a rate of 2.0 liter/min for 30 min at a height of 1.2–1.5 m from the floor.

5. Analysis

Mouth rinse and the collection medium were analyzed using ion chromatography (DRI-DHEM 100, FUJIFILM Medical Co., Ltd., Tokyo, Japan). Flame atomic absorption spectrometry (HITACHI Co., Ltd., Tokyo, Japan, 508) was used for the quantitative analysis of calcium and magnesium. The pH electrode method (HORIBA Co., Ltd., Kyoto, Japan, F-12) was used for the measurement of pH levels. The SPSS 17.0J (SPSS Japan Inc., Tokyo, Japan) and Microsoft Excel 2007 were used for the data analyses and graphic preparations.

Results

Figure 2 shows the measurement results for sulfuric ion, calcium, magnesium, Ca/Mg, and pH levels in mouth rinse collected from each of the 40 employees working with sulfuric acid, the 8 employees who work in the same plant but do not work with sulfuric acid, and the 8 general staff. The employees working with sulfuric acid exhibited the highest concentrations of calcium and sulfuric ions.

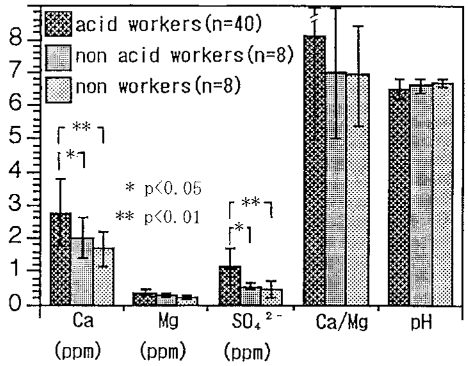


Fig. 2 Ca, Mg, SO_4^{2-}, Ca/Mg, and pH levels in mouth rinse of employees working with sulfuric acid, employees not working with sulfuric acid, and general staff

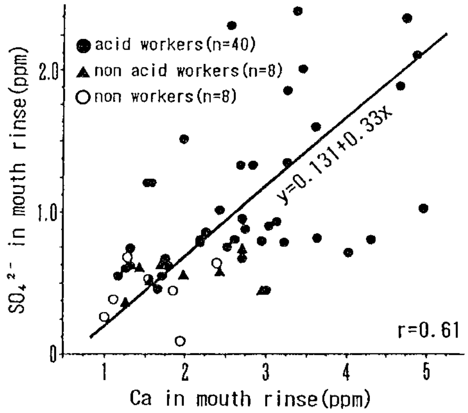


Fig. 3 Relation between Ca and SO_4^{2-} levels in mouth rinse of employees working with sulfuric acid, employees not working with sulfuric acid, and general staff (n = 56)

Table 1 Correlation coefficients matrix

	pH	Ca/Mg	SO_4^{2-}	Mg
Ca	−0.13	0.64***	0.61***	0.61***
Mg	−0.32**	−0.15	0.55***	
SO_4^{2-}	−0.31**	0.24		
Ca/Mg	0.16			

**: p<0.01, ***: p<0.005

Table 2 Variations in Ca, Mg, SO_4^{2-}, Ca/Mg and pH levels in mouth rinse of employees working with sulfuric acid

	Worker A before/after	Worker B before/after
Ca (ppm)	1.24/2.61	1.88/2.94
Mg (ppm)	0.26/0.26	0.31/0.28
SO_4^{2-} (ppm)	0.59/1.93	0.95/2.40
Ca/Mg	4.77/10.04	6.05/10.69
pH	6.75/6.21	6.78/6.01
SO_4^{2-}-Air*	0.13/0.78	0.13/0.84

SO_4^{2-} levels in working environment

	Acid working (n = 13)	Non acid working (n = 5)
mean	1.10 ± 0.64 mg/m³	0.43 ± 0.03 mg/m³
meanG	0.95 mg/m³	0.43 mg/m³

*: personal air sampler (mg/m³), G: Geometric

Significant differences were found in levels of sulfuric ions between those employees who were working with sulfuric acid and those who were not. Table 1 shows sulfuric ion, calcium, magnesium, Ca/Mg, and pH levels in the mouth rinse collected from each of the 56 subjects. Figure 3 shows a positive correlation between sulfuric ion concentration (which can cause dental erosion) and calcium concentration ($r = 0.61$, $p < 0.005$). Positive correlations were also found between calcium and magnesium concentrations ($r = 0.61$, $p < 0.005$), between Ca/Mg and calcium concentrations ($r = 0.64$, $p < 0.005$), and between sulfuric ion and magnesium concentrations ($r = 0.55$, $p < 0.005$). A negative correlation was found between sulfuric ion concentrations and pH levels ($r = -0.31$, $p < 0.01$), and between magnesium concentrations and pH levels ($r = -0.32$, $p < 0.01$).

Table 2 shows sulfuric ion, calcium, Mg, Ca/Mg, and pH levels in the mouth rinse collected from Worker A and Worker B at before and after work, and also sulfuric ion concentrations in the work environment as determined by the personal air samplers. The pH levels increased in acidity as time at work progressed, as did the other measured values. The sulfuric ion concentration in the work environment of the battery-charging area of the plant was approximately twice that of the other work environments investigated.

Sulfuric acid concentrations were measured in 13 workplaces in which sulfuric acid was present and in 5 in which it was not, with concentrations averaging $1.10 \pm 0.64\,mg/m^3$ and $0.43 \pm 0.03\,mg/m^3$, respectively.

Discussion

Dental erosion from the mandibular anterior teeth occurs frequently, and the level of pH in the saliva immediately after exposure to acid reflects the acid concentration in the work environment. It was reported that a combination of acid-induced direct decalcification of the tooth surface and abrasion through lip movement increased saliva calcium concentration, thus increasing the amount of urinary calcium excretion[13,15].

It is believed that saliva calcium concentrations in workers can be used as an index for measuring exposure to sulfuric ions in the work environment. In an earlier study, we reported that cadmium concentrations in the saliva and mouth rinse of employees working with cadmium had a high correlation with the work environment, and that mouth rinse could be used as an index for individual exposure[17].

In our earlier study[18], sulfuric ion concentrations in mouth rinse obtained from employees working with sulfuric acid were approximately twice those of employees not working with sulfuric acid. The average sulfuric ion concentration in the work environment of the battery-charging area of the plant was approximately double that of the other work environments investigated. These results suggested that mouth rinse reflects sulfuric ion concentrations in the work environment.

In another study[5], solutions were analyzed for Ca, P, Na and Mg. A substantial increase in the Ca/P ratio in the solution after approximately 6 hr of decalcification was ascribed to brushite formation. The ratios of liberated Ca/Na, P/Na, Ca/Mg and P/Mg were lower than the corresponding ratios in healthy enamel. This suggested that precipitation of brushite and preferential dissolution of Na and Mg compounds from enamel both play a role in dissolution-precipitation reactions in dental enamel during acid erosion.

LeGeros *et al.*[12] investigated Mg and CO_3 distribution in the outer (surface), middle, and inner (closest to the enamel-dentin junction, [EDJ]) layers of human enamel, the factors affecting the incorporation of Mg into synthetic apatites, and the consequences of such incorporation on the properties of those apatites. Their results demonstrated that concentrations of Mg, CO_3, and organic components increased from the surface to the inner layers close to the EDJ, and showed a difference in crystallinity from the outer to the inner layers.

In this study, we found calcium concentrations in mouth rinse to be significantly different among the employees working with sulfuric acid, the employees not working with sulfuric acid, and the general staff. Therefore, we speculated that this could indicate changes in oral calcium concentration and decalcification of tooth enamel when sulfuric acid vapor is inhaled into the oral cavity.

Our original hypothesis[18] was that sulfuric ions would cause decalcification of the tooth enamel and significantly increase calcium concentrations in the mouth-rinse samples. However, no radical differences were found in calcium concentrations in the mouth rinses obtained from employees working with sulfuric acid and in those obtained from general staff. Numerous studies on recalcification[11] in the oral cavity have found decalcification and calcification of enamel to be a common phenomenon, and this has led us to reconsider our original hypothesis. Because the ratio of magnesium in a tooth is approximately the same as the ratio of calcium in a tooth, magnesium was considered as a possible alternative to calcium[18]. In this study, although a tight correlation was expected between the sulfuric ion density and the pH, the obtained correlation coefficient was -0.31 ($p<0.01$), which we considered was due to the buffer action of acid caused by saliva in the mouth rinse.

Conclusions

In the present study, mouth rinse was collected from employees working with sulfuric acid in order to determine the level of individual exposure to sulfuric ions in the work environment, a substance that can cause dental erosion. Further study is needed in regards to calcium concentrations in mouth rinse samples from employees working with sulfuric acid. However, we believe that a more accurate indicator of individual exposure based on the relationship between calcium concentration and sulfuric ion concentration may become available in the future.

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