# INDUSTRIAL FLUORIDE POLLUTION IN THE METALLURGICAL INDUSTRY IN CHINA

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SUMMARY: The hazard of airborne fluoride pollution in 63 plants in the metallurgical industry in China was studied. Fluoride injuries to plant workers were most severe in the electrolysis works in aluminum plants and iron smelters. The incidence of fluorosis among workers was 3.2%, and the symptoms were systemic. For diagnosis, both the effects of airborne fluoride pollution and fluoride content in water must be considered, because some workers come from areas where fluoride content in water is high and fluorosis is endemic. Anti-air-pollution devices are needed to reduce the hazard of industrial fluoride pollution.

KEY WORDS: China; Dual effect; Hazard; Industrial fluoride; Industrial fluorosis.

## Introduction

Because fluoride is used extensively in industry, airborne fluoride has not only polluted the air and water supply but also adversely affected humans and cattle as described earlier by Roholm (1). Waldbott states: "Since fluoride is one of the most prevalent air pollutants, contaminated air and regionally contaminated food are likely to play an important role in soft tissue storage . . . ." (2). Reports on the hazard of industrial fluoride are available from many countries (3). To evaluate fluoride problems in China, we investigated industrial fluoride pollution in the metallurgical industry in China between 1980 and 1984.

## Materials and Methods

Air samples were taken from inside workshops of 63 fluoride-emitting plants in the metallurgical industry and their surroundings. Altogether, 9624 factory workers participated in the study, which included 3500 workers who underwent dental examination, electrocardiograms (2939 workers), skeletal x-rays (6224 workers), urinary F analysis (9422 workers), and hair F analysis (839 workers). For controls, 400 non-fluoride workers were randomly selected. Industrial fluorosis was diagnosed among workers according to Diagnostic Criteria (4).

## Results

Fluoride pollution monitoring data (Table 1) indicate that pollution from combined iron-ore, which contained 5-11% fluoride, was the most hazardous to plant workers and the surroundings because numerous cattle suffered from

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**Table 1**

Fluoride Pollution at 63 Industrial Plants

| Types of Plant | Workplace: Range of Mean F Level ($mg/m^3$) | Workplace: Times Above Criteria* | Outside: Range of Mean F Level ($mg/m^3$) | Outside: Times Above Criteria** |
|---|---|---|---|---|
| Electrolysis of Alumina (Large Scale) | 1.48-8.53 | 0.48-7.53 | 0.05-0.44 | 6-62 (Leeward of workshop 100-500 m) |
| Electrolysis of Alumina (Small Scale) | 0.40-3.36 | 0-2.36 | 0.02-0.09 | 2-12 (Leeward of workshop 100-500 m) |
| Iron Ore mixed with Fluoride | 0.40-9.94 | 0-8.94 | — | — (Pollution reached 50 km) |
| Steel Making (Fluorspar is used) | 0.63-1.58 | 0-0.58 | 0.004-0.05 | 0-6 (within a radius of 100 m) |
| Special Steel Making (Fluoride is used) | 0.03-18.12*** | 0-6.25 | 0.006-0.05 | 0-6 (within a radius of 100 m) |
| Cryolite Synthesis | 1.40-4.95 | 0.40-3.95 | 0.014-0.58 | 1-82 (Leeward of workshop 500 m) |
| Special Steel Making (HF is used) | 4.78-5.64*** | 0.91-1.23 | 0.004-0.007 | 0 |
| Manufacture of Phosphate Fertilizer | 0.10-28.0*** | 0-10.21 | — | — |
| Manufacture of Monocrystalline Silicon (HF is used) | 0.04-0.46 | 0 | 0 | 0 |
| Lead Electrolysis | 0.25-4.17 | 0-3.17 | — | — |
| Electric Welding | 13.1-26.9 | 4.25-9.76 | — | — |

* Criteria levels in workshops: HF 1 $mg/m^3$; Total Fluoride, 2.5 $mg/m^3$ (5).
** Criteria levels in atmosphere: HF 0.007 mg/day, Mean Value
*** Showed by total fluoride.

fluorosis within 50 km of the plant. Pollution in the electrolysis of alumina was mostly due to the use of open "Vertical Stud Soderberg Cells." In particular, high amounts of HF and other fluorides were emitted from large-scale electrolysis plants. In some small scale electrolysis plants, scrubber and exhaust gas retrieval systems were used to reduce F emission. Hydrofluoric acid is used in the synthesis of cryolite. Since the facilities where fluoride emission occurred were insufficiently sealed, pollution of the surrounding area was as serious as that with large-scale electrolysis. Although manufacture of phosphate fertilizer and of special steel causes F levels to rise to 28.0 and 18.12 $mg/m^3$, respectively, the period of production and workers' exposure to fluoride was shorter, the effect was less damaging. Except for the above-cited, because the number of affected workers was smaller and/or the pollution was less severe, the hazard of industrial fluoride was less marked in lead electrolysis, special steel, and monocrystalline silicon maufacturing plants. In electric welding, fluoride was emitted because of the use of welding rods which contained 8-40% $CaF_2$. Since F exposure was intermittent and since F containing welding rods were only selectively used in the steel making processes, the effect on workers were reduced. Table 2 shows the clinical data obtained from 9624 workers and 400 non-fluoride controls.

Table 2

Clinical Manifestations of Plant Workers and Controls

| Clinical Manifestations | Percent[1] Fluoride Workers (9624 Cases) | Percent[1] Controls (400 Cases) | p |
|---|---|---|---|
| Neurasthenia syndrome[2] | 34.9 | 21.8 | *[3] |
| Cough | 27.4 | 17.6 | * |
| Abdominal pain | 28.4 | 12.4 | * |
| Backache | 40.5 | 18.6 | * |
| Restricted joint movement | 11.0 | 2.7 | * |
| Chronic nasopharyngitis | 33.5 | 19.3 | * |

[1] Percent of population with positive manifestations of symptoms.
[2] Includes headache, dizziness, fatigue, insomnia, etc.
[3] * $p < 0.01$

Length of employment of the 9624 workers, aged 18-70 years (average 34), was 3 mo. to 36 yrs, with the majority ranging from 10-20 years. Clinical manifestations were significantly different between the two groups. Analysis of clinical data on 1020 workers revealed that prolonged exposure was associated with increased frequency of clinical manifestations. For example, restricted joint movement was revealed in 4.5%, 27.7% and 32.2% of those employed for 5, 15 and 25 years, respectively. Frequency of chronic nasopharyngitis in some potmen (large scale) was as high as 60.5%, due to prolonged irritation of the nasopharynx mucosa. In contrast, frequency shown by some HF acid washing workers was as low as 20%, possibly because of the lower F levels maintained in the workshop.

Regarding the dental examination, in 22% of the 3500 workers the corroded appearance on the surface of the teeth, might have been caused by HF acid erosion. In aluminum plants located in areas where fluoride content in water was high enamel mottling occurred in 65.9% of the 1500 native workers, compared to 61% among non-fluoride controls from the same area. Enamel mottling in controls may be the result of exposure to fluoride prior to employment (6,7).

F levels in urine and hair: In the past, many have believed that the extent of fluoride poisoning can be determined by the level of 24-hour urinary fluoride or spot samples. In a study of individual cases, however, urinary fluoride cannot be used as a function of fluoride intake (8). In this study 9422 workers were sampled from 36 assorted plants; urinary F content in pre-shift samples were compared with those in 1200 non-fluoride controls. Mean values of fluoride workers (0.3-7.5 mg/L) were higher than those in non-fluoride controls (local mean values 0.25–1.8 mg/L) which indicates that urine excretion was the main route for eliminating excess fluoride from the body and reflected the body burden of fluoride. In addition, some individual's post-shift urinary F content was as high as 21 mg/L, suggesting that post-shift urinary F could indicate the extent of fluoride exposure (9). By use of Spearman's Method, the correlation between the F level in workshops and urinary F content in operators was significantly positive for 2373 workers from 19 plants ($r = 0.69$, $p < 0.01$). Thus urinary fluoride may be used to determine individual body burden and appraise exposure of workers. Waldbott earlier reported that fluoride-induced injury could not be reliably determined on the basis of the level of urinary fluoride and that spot samples or single 24-hour samples of urine could be very misleading (10).

The F content in the hair of 839 workers (range 15-3884 ppm) was compared with that of 330 non-fluoride controls (range 20-85 ppm), and the difference between the two groups was significant ($p < 0.01$). However, no correlation was found between clinical findings, skeletal damage and F content in the hair samples. In chronic industrial exposure, the fluoride content of hair is likely to be a useful indicator of fluoride absorption (11).

Electrocardiogram changes in workers: Routine ECG check-up (using 9 leads) was carried out on 2939 workers and the abnormal frequency excluding primary heart and vessel diseases, was 46.6%. The frequency for the 150 non-fluoride controls, was 33.3% ($p < 0.05$). Analysis of abnormal ECG features revealed that over a third of the population showed sinus arrhythmia and/or bradycardia, the remainder had various conductive blocks, T wave changes ($V_3$,$V_5$), premature beats and myocardial ischemias. Whether the heart and arteries are damaged by fluoride or not (12-14), should be further investigated. Results of the analysis of radiograms of pelvis, forearms and lower legs are shown in Table 3.

With exception of the frequency of occurrence in coxarticular degeneration (Table 3: pelvis), significant differences ($p < 0.01$) in x-ray skeletal changes were found between the two groups. On the basis of x-ray films, osteosclerosis was the main change in industrial skeletal fluorosis, in agreement with Franke et al (3). Various degrees of increased density and trabeculae proliferations were observed in the pelvis. In order to determine the ossifiction of osteomembrane or interosseous membrane at forearm and lower leg, we used slightly underexposed photographs similar to the kind of radiography used for soft tissues (3); the existence of periosteal appositions could be established.

Table 3

Positive Radiological Findings in Skeletons of Workers Compared to Controls

| Radiological findings | Fluoride Workers (N = 6224) % | Non-fluoride Controls (N = 845) % |
|---|---|---|
| Pelvis: | | |
| Density increase | 10.57 | 0.39 |
| Trabeculae gauze-like[1] | 4.8 | 0 |
| Trabeculae linen-like[2] | 1.04 | 0 |
| Trabeculae marble-like[3] | 0.08 | 0 |
| Ossification on Obturatoria membrane | 25.40 | 16.60 |
| Ossification of iliolumbar ligament | 11.54 | 5.79 |
| Ossification of sacrospinosum ligament | 2.38 | 0.39 |
| Coxarticular degeneration | 5.27 | 8.88 |
| Tibia: | | |
| Increase in density | 5.91 | 0 |
| Trabeculae coarse | 12.35 | 2.33 |
| Ossification of osteomembrane or interosseous membrane | 21.19 | 8.67 |
| Knee articular degeneration | 14.93 | 2.67 |
| Radius and Ulna: | | |
| Increase in density | 4.88 | 0 |
| Trabeculae, coarst | 8.74 | 1.05 |
| Ossification of osteomembrane or interosseous membrane | 11.02 | 4.20 |
| Articular degeneration of elbow | 4.72 | 0.35 |

[1] Traceculae slightly coarse
[2] Trabeculae obviously coarse
[3] Trabeculae no longer discernible, bone structure white and marble-like.

In this investigation, a considerable number of workers suffered from endemic skeletal fluorosis because they came to us from an area where water F content as high. Dual effects from fluoride, which they suffered have been reported previously (6).

Diagnosis of industrial fluorosis: Based on Diagnostic Criteria (4), the total incidence of fluorosis in the studied population was 3.2%, 80% of which was in stage I; the age of the population ranged from 26-70 years (average 44.8 years); the period of occupational exposure ranged from 3-30 years (average 17.1 years).

Occurrence of the disease was related to the period of occupational exposure (Table 4); increased exposure period and increase in degree of fluorosis were directly related; after more than 20 yrs. of employment 47.7% of the workers were in stage 1, 73.3% in stage 2, and 100% in stage 3. After labor protection measures were adopted in 6 plants (Table 5), airborne F in workshops fell to permissible levels and fluorosis decreased to 0.7%. The highest incidence was 7.0% (potmen, large-scale pots), the lowest was less than 1% in furnace workers where fluorspar was used in steel making.

Table 4

Correlation Between Incidence of Industrial Fluorosis and Employment Period

| Employment Period (yrs.) | Incidence (%) |
|---|---|
| 5 | 5.0 |
| 10 | 23.8 |
| 15 | 31.5 |
| 20 | 43.7 |

Table 5

Correlation Between Incidence of Industrial Fluorosis and F Levels in Workshops

| No. of Plant | No. of Workers | Times above Critical Level | Incidence (%) |
|---|---|---|---|
| 9 | 2710 | 3.5-8.5 | 6.8 |
| 6 | 1637 | 0 | 0.7 |

## Discussion

Fluoride exposure by metallurgical workers was surveyed for the purpose of preventing the fluoride hazard. New technology in production processes, namely increased sealing of fluoride-emitting facilities as well as installation of ventilation and cleansing systems, tends to reduce fluoride pollution. Kaj Roholm (1), originator of modern fluoride research, outlined in detail the clinical manifestations of industrial fluorosis. Moreover, a vast amount of research (88 professional publications on fluoride from 1955 to 1983) was carried out by Waldbott on how fluoride affects the human organism.

The current investigation revealed that the total incidence of fluorosis was high because many of our workers were exposed in polluted workshops where F levels were above permissible limits for a prolonged period. For the purpose of diagnosis, occupational exposure must first be established. Some clinical symptoms are associated with the non-skeletal phase. Restriction of joint movements was frequently associated with abnormal findings in skeletal films. However, the classical symptoms of the non-skeletal phase of fluorosis were first delineated by Roholm. Walbott encountered the same symptoms prior to the onset of bone changes (15). According to our survey, clinical manifestations of fluoride injury were systemic (Table 2). A wide variety of vague, subtle symptoms occurred either prior to or simultaneously with the development of bone changes similar to those reported previously (16). Nonskeletal symptoms, therefore, are important for early diagnosis.

On the other hand, the dual effects of endemic and industrial fluoride should not be disregarded when the plant is located in an endemic area or the worker had been residing prior to employment in an area where the F level in water was high. Mottled enamel, a predominant sign, which develops only if the individual is exposed to fluoride early in life, contributes to differential diagnosis.

The diagnosis of industrial fluorosis cannot be established on the basis of urinary F data. No definite correlation was observed between urinary F levels, clinical stage, and neurological sequlae (17). Even among healthy workers we observed, as did Girakaja (18), F levels in urine could be higher than those in workers suffering from fluorosis. Factors affecting urinary F excretion include age, nutritional status, diet, kidney function, types of fluoride compounds, previous fluoride exposure, and many others (8). Thus, in the diagnosis urinary fluoride only indicates exposure to fluoride.

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