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Investigation and Study of Chromium Pollution in Jinzhou

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Abstract: Chromium pollution has existed in Jinzhou for twenty-five years. The long-term stockpiling of chromium-containing waste residue in the open air has resulted in long-term and continuous groundwater contamination. The use of large quantities of ferrous sulfate to treat chromium-containing waste water also led to man-made pollution, resulting in serious damage to agricultural crops and human health. In 1982, an underground seepage prevention wall was adopted as a control measure, and the anticipated effect has been attained.

Key words: Hexavalent chromium Chromium containing waste residue Ferrous sulfate

On January 26, 1965, the water quality of water in certain wells in the two villages of Nuerhe and Jinchangbao in the Taihe District of the Jinzhou suburbs turned yellow and became undrinkable. Field investigation confirmed that it was severe hexavalent chromium (Cr^{+6}) pollution.

I. Pollution Source

The source of the Cr^{+6} pollution was the Jinzhou Iron Alloy Plant. This plant began trial smelting of metallic chromium in 1959, began small scale production in 1961 (with a recovery rate of only 24.5% at that time, large amounts of chromic salts were leached off), and began mass production in 1965, resulting in a dramatic increase in Cr^{+6} containing waste water, which reached a maximum of 125 t/h (with maximum Cr^{+6} concentrations in leached wastewater of 105 mg/L; after precipitation processing, the concentration remained around 20 mg/L), all of which drained into an open ditch outside the factory that emptied into Xiaobagou, a dry fossil riverbed. During the production process, large volumes of chromium containing vapor also diffused into the atmosphere. Since production began, waste residue had first been placed in bulk in empty spaces inside and outside the plant. When it was discovered that this caused contamination, waste residue was stockpiled in a central location outside the factory. By the 1970s, the log-term accumulation of residue had exceeded 300,000 tons covering an area of 50 *mu*[1], known as the residue heap. Exposure to wind and precipitation year after year led to the leaching of large amounts of Cr^{+6} into the ground. Thus this pollution case was the result of a complex and persistent contamination event involving the gas phase, the liquid phase and the solid phase.

II. Contamination Process

Contamination began in 1960, manifested primarily as groundwater contamination. With the chromium production workshop as the starting point, a highly concentrated polluted area was formed in the same direction as the flow of groundwater. In early 1965, the scope of the pollution was limited to the central areas of the two villages of Nuerhe and Jinchangbao (28.2% of wells were contaminated; the well water in 54.67% of them had Cr^{+6} content in excess of 20 mg/L). By the end of the year, it had spread downstream to the Nuerhe Train Station, Yangxingtun, Shilitai, Wenjiatun and Bajiazi, expanding the area of the pollution zone to 10 km^2. By early 1966, it had spread 9 km from the pollution source to Jinzhou's Nanshan waterhead (the primary source of drinking water for Jinzhou, primarily fed by the Nuer River). In May 1966, the Cr^{+6} content in this waterhead was 0.003 mg/L; in 1969, it was 0.004 mg/L. By 1974, the polluted area had spread to cover an area of 22.5 km^2, forming a long, narrow pollution zone along the periphery of the old river course, and was continuing to spread in all directions.

Beginning in 1965, a variety of control measures were adopted with minimal effect (Table). As years of investigation have proven, the reason for this is that Cr^{+6} containing waste water was only the original cause of contamination, while the continuation and spread of the contamination over the long term were caused by the stockpiling of chromium containing waste residue. By 1966, the Cr^{+6} content of waste water discharged by this plant had fallen to 3.0 mg/L, and although there were fluctuations each year, the volume seeping into groundwater from the ground surface was already quite low. According to investigations, a linear relationship existed between the Cr^{+6} concentrations in different well locations within the polluted area and the distance from the residue heap, the regression equation for which is

[1] Translator's note: *Mu* is a Chinese measurement of land area, equivalent to approximately one-sixth of an acre.

Table: Changes in Cr^{+6} Content in Different Locations of the Polluted Area in Various Years (mg/L)

Area	Distance from Pollution Source	Year					
		1965	1966	1969	1974	1976	1979
Jinchangbao-Nuer River	1.5	0.6-10.0			10.5		0.06-4.33
Shilitai-Yangxing Village	3-3.5		0.002-20.0		0.01-0.05		0.001-0.03
Wenjia Village-Bajiazi	5-5.5						0.003-0.004
Nanshan Waterhead	8.5		0.001-0.003	0.002-0.004		0.002-0.004	Trace-0.014
Nuer River river water	1.5		0.01				0.167-0.99

$C = 40.46e^{-7.94\times10^{-4}x}$. The residue heap had 300,000 tons of existing chromium residue. The Cr^{+6} content of new residue averages 1.55%, while the content in older stockpiled residue is 0.34%. Cr^{+6} content in the soil layer beneath the residue lot reached maximums of 4,700 mg/kg, and it is estimated that the residue heap transferred approximately 0.3 tons of Cr^{+6} into groundwater daily. It was only when a concrete anti-seepage wall was installed in 1980-1982 to rein in contamination that Cr^{+6} pollution of groundwater was alleviated.

III. Pollution Damage

1. Impact on agricultural crops: The area of Cr^{+6} pollution is Jinzhou's primary vegetable growing region. Average concentrations of Cr^{+6} in vegetable field irrigation wells range from 0.006-0.739 mg/L, and the irrigation area covers 1,800 *mu*. According to investigations made in 1982-1983, Cr^{+6} contents in irrigated soil were 62.5-67.5 mg/kg, while uncontaminated reference (background) values were 59.5-61.5 mg/kg. For many years, crop yields in the vegetable growing area decreased, and Cr^{+6} contents in vegetables exceeded those in the reference area. For example, the Cr^{+6} contents of Chinese cabbage and green cabbage in the polluted area were 0.025±0.015 and 0.014 ±0.0056 mg/kg, respectively; reference area values were 0.011±0.001 and 0.007±0.0025 mg/kg. The variances between the polluted area and the reference area had pronounced significance ($P < 0.05$) after *t* tests. Additionally, there was a positive correlation between the Cr^{+6} contents of the same vegetable variety and corresponding Cr^{+6} concentrations in the water used to irrigate them ($y = 0046x + 0217$, $r = 0.8844$).

2. Damage to human health: According to a 1965 survey of 155 people in the village of Nuerhe who had directly drunk groundwater containing high concentrations (20 mg/L) of Cr^{+6}, symptoms including perleche, diarrhea, abdominal pain, indigestion and vomiting appeared. Elevated white cell counts, elevated juvenile cells among neutrophilic granulocytes, and shifts to the left appeared in residents of highly polluted areas. Results of surveys of Shilitai in 1971 and Wenjiatun and Sandaohao in 1974 were similar.

According to a retrospective investigation of the causes of death for populations in the polluted areas from 1970-1978, malignant tumor mortality rates (adjusted; the same applies below) for residents located in the polluted area were 71.89-92.66/100,000, while the mortality rate in Taihe District for the same period was 65.40/100,000. Lung cancer mortality rates between 13.17-21.39/100,000, while the average for the entire district in the same period was 11.21/100,000. Stomach cancer mortality rates were 27.68-55.17/100,000, also higher than the average for the district as a whole, with signs of increasing malignant tumor mortality rates as proximity to the pollution source increases. Animal experiments have also shown that Cr^{+6} can cause an increase in the rate of chromosomal aberration in the bone marrow of white laboratory mice (Zhang Jiandong, et al., "Experimental Observation of Hexavalent Chromium Induced Chromosomal Aberration in Laboratory Mice," *Chinese Journal of Public Health* [*Zhongguo gonggong weisheng zazhi*], 1986:5(4):49). The potential damage to human health of Cr^{+6} pollution is undeniable.

IV. Experience and Lessons Learned Through Cleanup Process

In the process of cleaning up the pollution, contamination of groundwater by Cr^{+6} containing waste water was the first thing noticed. As a result, the control measures adopted consisted primarily of improving calcination, preventing ground seepage, centralized stockpiling of waste residue and the imposition of ferrous sulfate treatments. Pre-discharge waste water underwent treatment in ferrous sulfate and precipitation together with lime. Polluted

groundwater was intercepted and treated with ferrous sulfate. The ground surface within the plant area was treated using ferrous sulfate infiltration purification methods. After these measures, beginning in 1967, the concentration of Cr^{+6} in the groundwater fell quickly. However, because the various control measures were targeted at Cr^{+6} containing waste water, and the primary means involved the use of large amounts of ferrous sulfate, cleanup of the waste residue was overlooked, causing the residue to form a source of massive, persistent pollution of groundwater and soil while also resulting in irreversible manmade contamination of the groundwater with sulfates. Sulfate and chloride contents in the water in the Nanshan waterhead rose each year beginning in 1967, and the hardness of the water changed suddenly and continued to increase. In 1965, water hardness remained below 100 mg/L. By 1980, it had reached 199.26 mg/L. Chloride content was only 20-22 mg/L in 1966; by 1980, it had exceed 80 mg/L. Sulfate content rose from 20-30 mg/L in 1967 to 100 mg/L in 1980, and by 1982, it had risen further to 122.3 mg/L. Sulfate content of well water within the polluted area was generally 250-300 mg/L, with an individual peak value of 966 mg/L.

V. Residue Heap Cleanup and Evaluation of Results

In 1982, an underground concrete anti-seepage wall was built around the residue heap, and the body of the wall was inserted into bedrock, sealing the 300,000 tons of chromium residue in a large concrete enclosure. Over two years of constant observation proved that the anti-seepage wall produced marked results in curbing the continued contamination of groundwater (Wang Caizhang, "Application of Concrete Anti-Seepage Wall to Control Chromium Pollution," *Jinzhou Environmental Science and Technology* [*Jinzhou huanjing keji*], 1985: (1): 26). Yearly average Cr^{+6} content in the observation well outside the wall fell from 18.15 mg/L in 1981 to 4.30 mg/L in 1983. Yearly average Cr^{+6} content in the observation well inside the wall rose from 189 mg/L in 1982 to 453.85 mg/L in 1983. Cr^{+6} contents in the groundwater at various locations within the polluted area also fell each year, decreasing an average of 26-33% from 1982 to 1983, and the incidence of measurements in excess of standards fell by 20-40%. The chromium contamination that persisted for twenty years is now gradually being controlled and eliminated.

[English abstract]

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