

# Chromium Contamination in the City of JinZhou

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## Preface:

On January 26, 1965, there was a report that the drinking water in some wells of Nuer village and JinChangBao village, suburbs of JinZhou city (TaiHe District), had turned yellowish. Residents asked for an investigation. JinZhou Health and Anti-Epidemic Station conducted a field investigation immediately and confirmed that water in some wells had turned yellowish (green while cooking) and was undrinkable. As reported by residents, water quality had been changed for nearly half a year, but only sparked their concern when the yellow color of the water became strongly noticeable. The field investigation confirmed that underground water had been heavily contaminated with hexavalent chromium. In the following 20 years, related institutions have conducted much investigation into the causation, severity, and effect of the contamination on the environment and human health, as well as into treatment to the contamination. Now the causation and development of the contamination are clear.

This hexavalent chromium contamination is rare in the world, due to its great contaminating range, severe damage, and endurance. During the past 20 years, related institutions have accumulated many important documents in the process of investigating, observing, and treating the contamination. The institutions have had both successful and unsuccessful results. Now we can summarize the entire event in order to get helpful experience and discuss possible study projects for the future.

## Pollution Source:

The source of this hexavalent chromium contamination is JinZhou Alloy Corporation. Built in

**Table 1 Concentration\* of Chromium in the Contaminated Area**

Location	JinchangBao Nuer Village	Shilitai YangXing	Wenjiatun Bajiajie	Nanshan Reservoir	Nuer River
Distance to Alloy Plant	1.5km	3-3.5km	5-5.5km	7.5km	1.5km
1965	0.6-10.0				
1966		0.002-20.0		0.001-0.003	0.07
1969				0.002-0.004	
1974	70.5	0.01-0.05			
1976				0.002-0.004	
1979	0.06-4.33	0.001-0.03	0.003-0.004	0.014	0.167-0.99

\*Concentration is measured by mg/L

the 1940s, the company started to work on hexavalent chromium smelting in 1959. In 1961, the company began a small amount of production (only 24.5% of hexavalent chromium was recovered at the time). The rate of recovery increased to 56.3% in 1963 and then remained at 60% for many years. The low recovery rate caused a large amount of chromate discharge. Regular production began in 1965, at which time sewage containing hexavalent chromium also dramatically increased. The maximum discharge rate was 125 tons per hour. The maximum hexavalent chromium concentration was 105mg/L. Before sedimentation, the hexavalent chromium concentration was 79mg/L. Even after sedimentation, the hexavalent chromium concentration remained at the level of 20mg/L at the end of the discharge pipe. All the sewage was discharged into an open ditch by the plant. In the meantime, there was also a large amount of hexavalent chromium vapor disseminated in the surrounding atmosphere in the process of smelting. The ore residue (approximately 1500 tons) was scattered on open ground in or near the plant. Due to poor management, there were more than 30 leaking parts in the equipment.

After accumulating for five years, and because of the special geological environment of the plant, air, water, and soil contamination became strongly noticeable. The water contamination was the key characteristic among these three.

The geological characteristic of the location of JinZhou Alloy Corporation is the first factor of this contamination. The hexavalent chromium contamination zone is located on the north bank of Nuer River, which is low hills with decayed bedrock that is developing cracks. Because of its high altitude, this location is a supplying region for underground water. The water-containing layer is gravel clay. It has a thickness of three to nine meters and is located one to four meters underground. The direction of the underground water movement is southeast. The permeable coefficient of earth soil layer is 150-200 meters/day. The speed of the movement is 0.162 meters/hour.

Most of the sewage containing hexavalent chromium was discharged into an open ditch, whereas a small amount permeated into the soil inside the plant. The southeast flow of sewage merged into the old course of the Nuer River,(Figure 1) which is dried. Hexavalent chromium being

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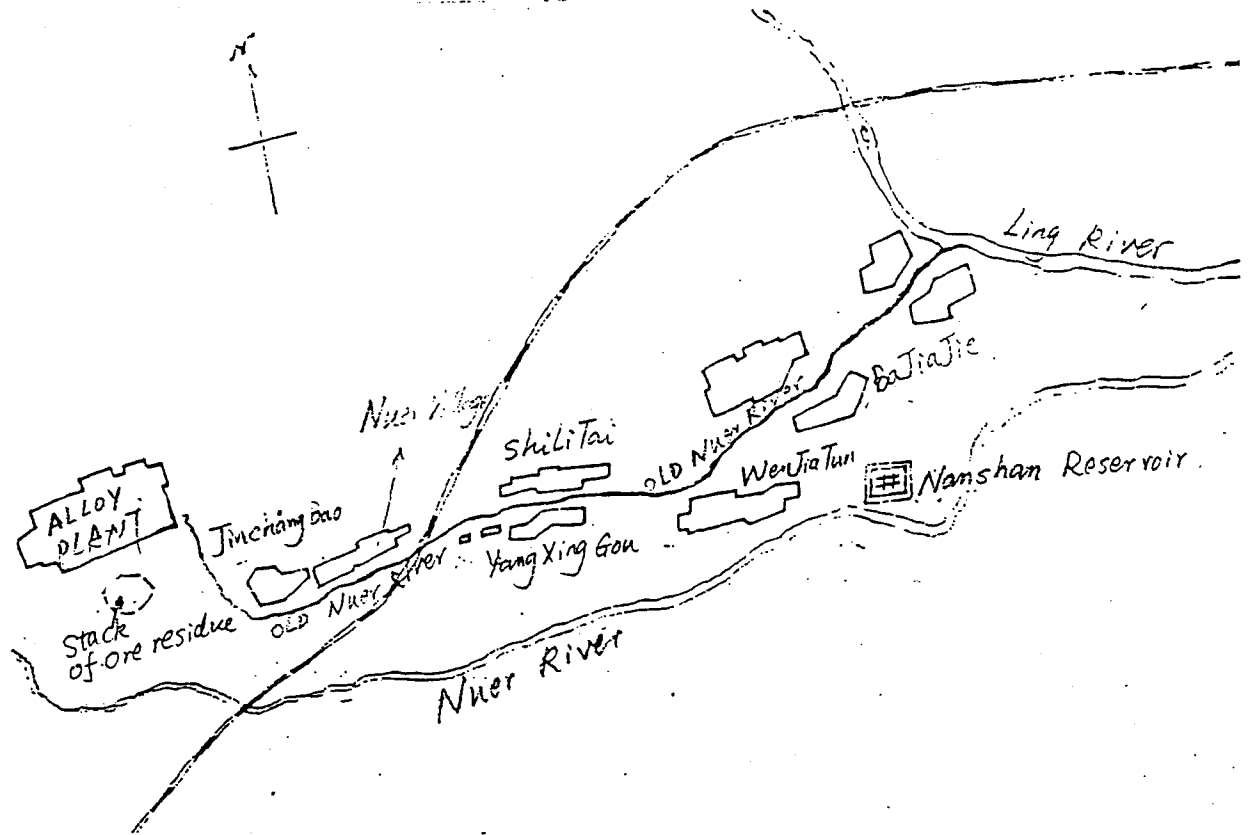


Figure 1: The Map of the Location of villages and rivers

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discharged from the plant and permeating into the soil is the second factor of this contamination.

Noticing the contamination, the company concentrated the scattered ore residue on open land located to the south of the plant. The stacks of ore residue now occupy 50 mu (1mu =0.0667 hectares). The basement of the original dump sight was made by cement and covered by asphalt and oil felt, to prevent permeating. Walls were built around the dump site so as to protect it. The original dump site has been buried in the center of the hugh stacks of ore residue, which are more than 300,000 tons this day, compared to 1,500 tons in 1965. The effort of preventing permeation has lost its usefulness. Ore residue containing hexavalent chromium, which was melted with the rain and spread by wind, caused hexavalent chromium to transfer into the soil. This is the third factor for the contamination.

### **Process and Effect of the Pollution:**

#### *Section 1: Process*

Based on the field investigation, the contamination of underground water came from the leakage of the plant. The range and severity of the contamination changed over the 20 years. Sewage and ore residue have exchanged their importance as the causation of this contamination.

Starting in 1960, this contamination limited to central area between Nuer village and JinChangBao village in 1965. (Figure 2A)

Results from observing wells in 1965 indicated that contamination of underground water, starting from the plant, formed a contamination region concordant with the movement of underground water. The contamination region, caused by leakage and permeation, has a trough shape. Hexavalent chromium concentration is high in the middle of the cross-section of the trough, lower on both sides, contrary to the altitude of the underground water. The gradient of the underground water limits the hexavalent chromium horizontal proliferation and eventually forms

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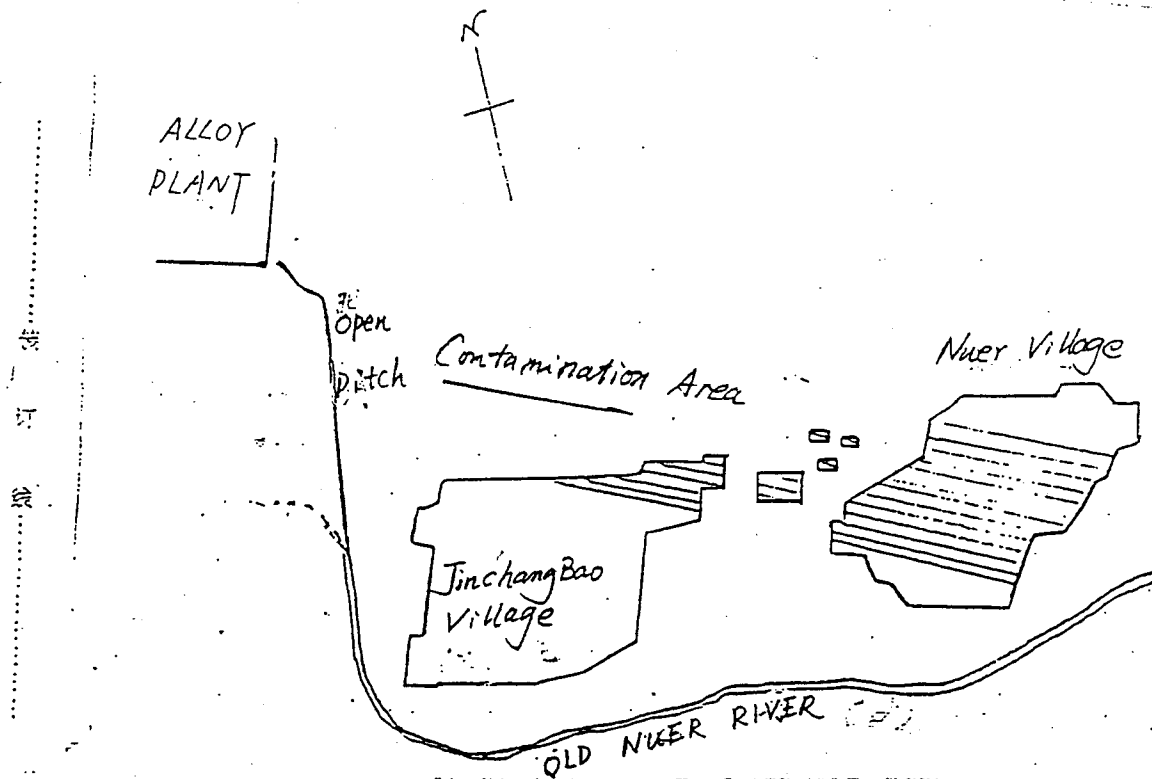


Figure 2: 1965 Contamination Area

a long and narrow contamination region. The first victim was Nuer village.

At the beginning of 1965, 75 water wells (28.2%) contained hexavalent chromium among 266 water wells in Nuer village and JinChangBao village. The highest concentration was 10mg/L, lowest was 0.6mg/L. Among those, 41 wells (54.69%) had concentration more than 2.0 mg/L.

By the end of 1965, underground water contamination had been expanding to half of the JinChangBao village (40.65% wells contained hexavalent chromium), most of the Nuer village (95.88% wells contained hexavalent chromium). The underground water contamination further expanded to several other villages (Nuer Railway Station, YangXing, ShiLiTai, WenJiaTun, BaJiaZi) located down the Nuer River. The whole contamination region occupied 20 km<sup>2</sup>. Among 144 sample water wells selected from those villages, 92 contained hexavalent chromium. The highest concentration of hexavalent chromium was 5mg/L in the YangXing village and Nuer Railway Station, and for the others, the hexavalent chromium concentrations were lower than 0.05mg/L.

Besides the reasons mentioned above, one key reason for the contamination of the villages located down the Nuer River is that sewage containing hexavalent chromium permeated into soil of the old dried Nuer River bed. Because the old Nuer River bed became bare sand layer after the Nuer village, all the sewage permeated before the west of YangXing village. The bed of old Nuer River remains dried.

By 1966, the contamination had reached the Nanshan reservoir, the major drinking water source for JinZhou city, located 18 li (9 km) from the alloy plant. The concentration of hexavalent chromium in the Nanshan reservoir was between 0.001 and 0.002mg/L. The main supplying river for the Nanshan reservoir is Nuer River. Due to topographical reasons, underground water of old Nuer River flows into Nuer River in the yearly dry period. For this reason, water in Nuer River contained hexavalent chromium. In May 1966, the concentration of hexavalent chromium in Nuer River was 0.07mg/L, by which time the concentration of hexavalent chromium in Nanshan reservoir area was 0.002-0.003mg/L. In 1969, the concentration of hexavalent chromium in Nanshan reservoir was 0.002-0.004mg/L.

By 1974, the total area of contamination reached 45 li<sup>2</sup> (11.25 km<sup>2</sup>). The contamination area was a long and narrow region along old Nuer River, gradually expanding. The concentration of hexavalent chromium of underground water of Nuer Village and JinChangBao reached 70.5mg/L. Even ShiLiTai and WenJiaTun, the concentration reached 0.05-0.01mg/L.

In 1979, after a series of treatments, the hexavalent chromium concentration around the end of the discharging pipe dropped. Concentration was between 4.33-0.06mg/L in Nuer Village and JinChangBao. ShiLiTai and YangXing had concentration 0.03-0.001mg/L. Concentration was still as high as 0.014mg/L in newly contaminated villages. The concentration of hexavalent chromium in the Nuer River was 0.99-0.167mg/L. 1979 was the year with highest hexavalent chromium concentration in most remote areas. The trend and intensity of contamination before 1979 was expanding. After 1979, the contamination trend and intensity was declining. (see Table I)

Extensive investigations in the following years have disclosed that hexavalent chromium containing sewage may only have attributed to the initial contamination, whereas the stacks of ore residue have been the source of the long-term underground water pollution.

The pattern of this contamination is the following:

1. The sewage containing hexavalent chromium was discharged and permeated into the soil evenly. Due to immediate treatment by the company, the hexavalent chromium concentration in sewage decreased rapidly. By 1966, the concentration of hexavalent chromium in the sewage was reduced to 3mg/L. Although this concentration fluctuated during the next 20 years, the contaminating sewage became a steady small amount.
2. Compared to that, the stacks of ore residue have been the main source of the long-term underground water pollution. It has been estimated that the dump site had about 300,000 tons of dregs. For the new dregs the hexavalent chromium content was 1.55%, and for the old ones, the content was 0.34%. Hexavalent chromium accumulated in the soil and transferred into underground water because of the stack of ore residue that melted with rain. The highest



concentration layer is the clay layer with a thickness more than one meter. Because of low permeability and high density, the concentration of hexavalent chromium reached 4700mg/Kg. Underneath the clay layer is the water bearing formation which has high permeability. Rain water entered this layer directly so that the hexavalent chromium concentration became lower in it. It was estimated that stack of ore residue transferred approximately 0.3 tons of hexavalent chromium into underground water per-day.

3. Because the main source of contamination was the stack of ore residue, the hexavalent chromium concentration of water well had a linear correlation with the distance between the water well and the stack. The estimated regression equation is

$$\log C = 1.6065 - 3.4486 \times 10^{-4}x$$

$$C = 40.46e^{-7.94 \times 10^{-4}x}$$

The correlation is statistically significant; therefore the main cause of the long-term great range contamination was underground water contamination by the stack of ore residue.

4. The intensity of underground water contamination depends directly on rain and geological conditions. The hexavalent chromium concentration in the underground water around the waste site is high during the yearly period of abundant water, whereas the concentration in the remote area is high during the yearly period of drought. This fact indicates that in the yearly period of abundant water, both the supplying and exploiting amount of underground water is large. As such, the pollutant transfers rapidly, and the contamination area thus expands quickly. During the yearly period of drought, the exploiting amount of underground water is small, and therefore pollutant moves slowly. The above-mentioned phenomenon is a characteristic of this contamination.(Figure 2B)

The hexavalent chromium contamination expanded and intensified as a result of the accumulation of ore residue.(Figure 3) Only after an underground seepage prevention method was applied in 1980-82, the underground water hexavalent chromium contamination became moderate.

## Section 2: Effect on Crops

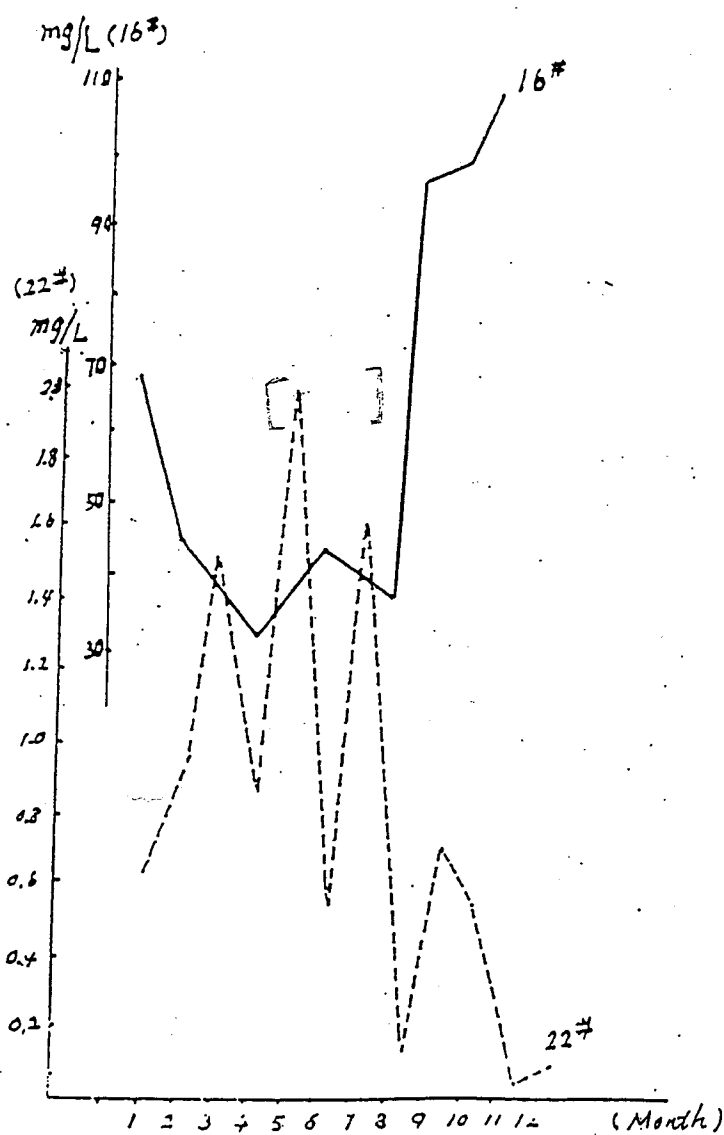
The polluted areas are the places where vegetables are the major agriculture products. The irrigation water for the vegetable fields came from the contaminated water well. Hexavalent chromium concentration of the irrigation water was high. The average concentration was 0.006-0.739mg/L. The irrigated area was about 1,800 mu (1mu=0.0667 hectares). Because of regular irrigation by contaminated water, hexavalent chromium had accumulated in the surface soil. Based on the investigation conducted in 1982-1983, the hexavalent chromium concentration in the fields irrigated by contaminated water was 62.5-67.5mg/Kg. This concentration was only 59.5-61.5mg/Kg in the fields irrigated by uncontaminated water. This fact indicates the hexavalent chromium accumulation in the vegetable fields was because of irrigation by contaminated water. This hexavalent chromium accumulation must have some biological effect on the vegetables grown on the fields. In fact, the hexavalent chromium concentration of the vegetables grown on the contaminated fields is higher than that on uncontaminated fields. (see table II)

Table II: Comparison of the Hexavalent chromium Concentration in vegetables Between Contaminated Fields with Uncontaminated Fields (mg/kg).

	Contamination Fields	Uncontaminated	t-test
Vegetables			
Cabbage ( )	0.025+ 0.015	0.011+0.001	p<0.05
Nappa ( )	0.014+0.0056	0.007+0.0025	p<0.05

Hexavalent chromium concentration in the vegetables is linearly correlated with the concentration in irrigating water. (Table III) The external hexavalent chromium allocation in the body of vegetables varies according to location: Roots have the highest load; leaves have a moderate amount; and fruits have a very small amount. In the pot plant experiment, crops' growth, development, and photosynthesis was largely affected by irrigation of chromium contaminated

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(2.2)  
Figure 2: Chromium Concentration observed by Observing Well #16 (under the Ore Residue Stack) and #22(Remote Area)

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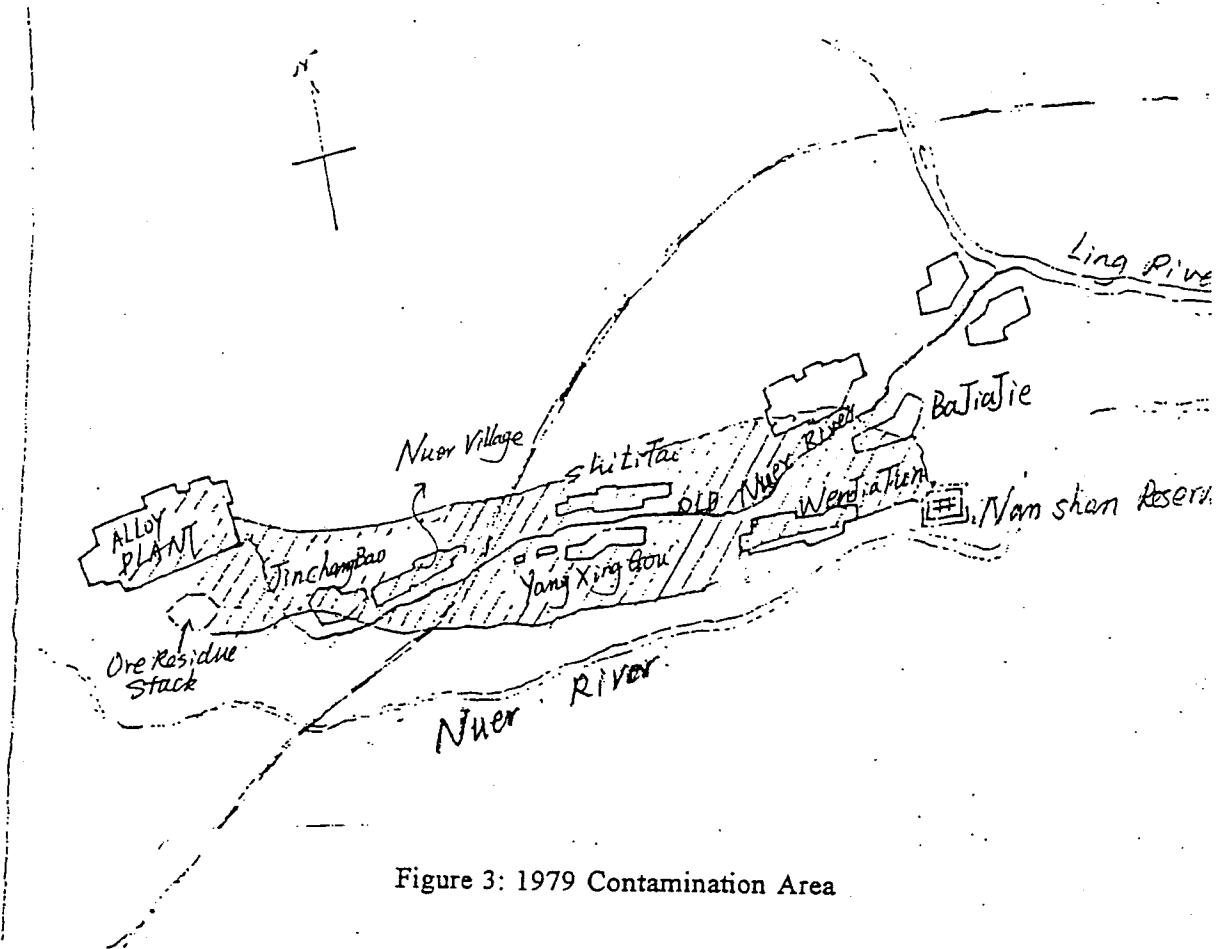


Figure 3: 1979 Contamination Area

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water. In fact, vegetable productivity in the contaminated area decreased. The effect of eating high density hexavalent chromium vegetables on human health is still an open question.

Table III Hexavalent chromium Concentration in Cabbage

Chromium Concentration in Underground Water (mg/L)	Chromium Concentration in Cabbage (mg/kg)
0.006	0.024
0.008	0.030
0.100	0.015
0.330	0.039
0.540	0.041
0.700	0.059
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$y=0.0463x+0.0217 \quad r=0.8844$	

### *Section 3: Effect of Hexavalent chromium Contamination on Human Health*

Because the hexavalent chromium-containing sewage directly polluted underground water at the beginning of the contamination, residents drank water with a hexavalent chromium concentration level much higher than the acceptable amount of drinking standard. In early 1965, some residents living in Nuer village and JinChangBao village developed oral ulcer, diarrhea, abdominal pain. After that, other villages in the contamination area, located further, had similar symptoms, even the most remote village (WenJiaTun) in 1974.

Regularly drinking water with high hexavalent chromium density for a long time may increase digestive symptoms incidents. A number of studies have shown the similar results. In a cross-sectional study conducted in 1965 in Nuer village, sampling 155 residents, 51 (33%) individuals developed oral ulcers; 26(17%) had diarrhea symptoms; 48(31%) had abdominal pain; 26(17%) had dyspepsia symptoms; 31(20%) had pain in the pit of their stomachs; and 20 (13%) had vomiting. A blood study with 12 subjects from high density contamination areas revealed that the white blood cell in study samples was higher than standard ( $5100-16300 \times 10^4 / \text{mm}^3$ ). (or leucocytosis). Another blood study with 93 subjects revealed that the number of neutrophilic

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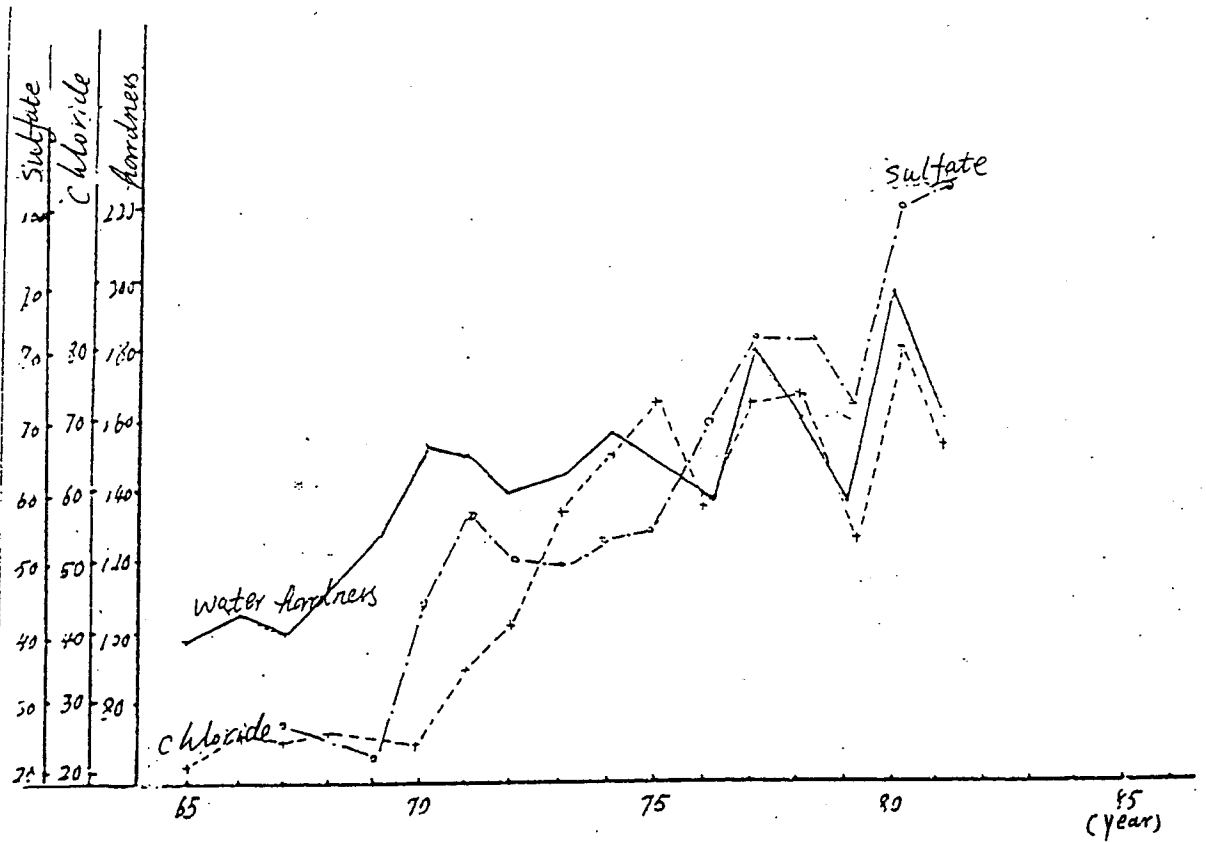


Figure 4: Water Quality of NanShan Reservoir

granulocyte and juvenile cells was higher than standard, and there was the tendency for the cell nucleus to shift left. At the time of this study, the hexavalent chromium concentration was 0.1-20.0 mg/L. The symptoms in the study were acute. They disappeared after the water quality was improved or after the human body accommodates to the environment.

In 1971, a cross sectional study with 158 subjects in the village of ShiLiTai showed the following results: 92(58%) individuals developed oral ulcers; 48(30%) had diarrhea; 36(23%) had abdominal pain; 16(10%) had dyspepsia symptoms. Although the results were similar to the Nuer village study, the hexavalent chromium concentration in the underground water was lower, at the level of 0.003-0.05mg/L. The concentration of sulfate, however, reached more than 300mg/L, with a maximum concentration of 900mg/L. These results and pollution conditions were similar to the results and conditions of other studies conducted in WenJiaTun and SanDaoHao in 1974. All of the above studies suggest that the pollution of sulfate may have a noticeable effect on human health.

A retrospective mortality study of the year from 1970 to 1978 of residents living in the contamination area showed that the malignant tumor rate for the contamination area (JinChangBao, Nuer River, YangXing, WenJiaTun) was 73.42-99.30/10<sup>5</sup> (adjusted rate was 71.88-92.66/10<sup>5</sup>), compared to the rate of 65.40/10<sup>5</sup> in JinZhou city. Lung cancer death rate in the contamination area was 13.17-21.39 /10<sup>5</sup> (the district average was 11.21/10<sup>5</sup>); and stomach cancer death rate in that area was 27.68-55.17/10<sup>5</sup>. This number was higher than district (TaiHe) average. This area was a high cancer incidents area of TaiHe district. The death rates as a result of malignant tumors shows some correlation with the distance of the village location to the plant: namely, the closer the village to the plant, the higher the death rate. This fact revealed that the hexavalent chromium contamination of water, soil, and crops might be correlated with higher tumor rate. In a rat experiment in 1980, it was confirmed that hexavalent chromium costs a higher chromosome aberration rate of bone marrow cell. This result suggests that Cr<sup>+6</sup> pollution must have its effect on human health.

#### **Treatment and Further Treatment Pollution:**

In 1965, after noticing the contamination, people began to notice its severity on contaminating the underground water. City Council of JinZhou stopped JinZhou Alloy Corporation's production for a period of time and made the following improvements:

(1) Improving the company's smelting procedures: The new procedure is ball-milling and cold water soaking, compared to the old procedure of alkali smelting and hot water soaking. This improvement prevents vapor contaminated with hexavalent chromium from evaporating into air.

(2) Improving the basement of the workshop, where hexavalent chromium-containing sewage(highest concentration was 105mg/kg) permeated into the soil . The improvements prevented such permeation. .

(3) Collecting 20,000 tons of ore residue ,which had been soaked, into space on open ground. Then built a ditch around the perimeter of the ore residue, and treated the ore residue with ferrous sulfate.

(4) Building a sedimentation pool at the end of the sewage discharge pipe. Before being discharged, ferrous sulfate and then lime cream were added to the sewage, to sediment.

(5) Building treatment wells: in the area where underground water was being contaminated, three treatment wells were built ( one north to JinChangBao, one north to Nuer Rive, one at east gate of the alloy plant). These wells were used to extract underground water, which then was treated with ferrous sulfate. Ferrous sulfate simultaneously was used to treat the surface soil in the plant.

After the above-mentioned treatments, the hexavalent chromium concentration of underground water quickly decreased after 1967; and it stayed steady through the next 20 years. The hexavalent chromium concentration of the Nanshan reservoir has been fluctuating in the a trace amount of 0.004mg/L.

The original treatment was adding ferrous sulfate to the sewage and adding ferrous sulfate to



extracted underground water. No measurement of how much sulfate should be added to treat the extracted water had been made before adding it. Sometimes water extracted by the treatment well was dumped directly on the ferrous sulfate and neglected. The results of this treatment were the following:

1. The stack of ore residue caused a long-term and great range contamination of underground water and soil.

2. Ferrous sulfate polluted the underground water. (treatment pollution)

Both of these two results are lessons we can take from the original treatments. Using Well Treatment can improve underground water quality rapidly and limit pollutant diluting. But the fact that the hexavalent chromium concentration reduced rapidly after the water extraction was stopped indicates that well treatment speeds up the movement of underground water and therefore increases the speed of pollutant transfer. Because a low pressure area was formed around the treatment well, it became difficult for the well to extract water. The treatment well method cannot be a reliable and effective way in the long run.

Because of the pollution of ferrous sulfate, the concentration of sulfate and chloride in the water of the Nanshan reservoir increased after 1967. The quality of underground water irreversibly deteriorated. In 1965, the hardness of the water was less than 100mg/L. By 1980, this number changed to 199.26mg/L. The highest hardness in some water wells were as high as 307.23mg/L. In 1966, the concentration of chloride was only 20-22mg/L, and by 1980, it was more than 70 mg/L. In 1966, the concentration of sulfate was only 20-30 mg/L, but by 1980 increased to 100mg/L. It increased again to 122.3mg/L in 1982. Average sulfate concentration in the wells located in contamination areas was 250-300mg/L. The highest concentration reached 830-966mg/L (JinChangBao village). This contamination caused health problems for many people. (see Figure 4)

#### Treatment to the Stack of Ore Residue:

The size of the stack of ore residue increased after it first built up. A large amount of hexavalent chromium was melted by rain and entered into soil, which caused a long-term great range contamination. Well treatment has been proven not to be very effective and has been stopped, although it has some effectiveness in limiting the spreading of hexavalent chromium. After 1980, it was suggested that ore residue can be used to make mixed cement material, by smelting with gangue and aluminum silicate under a temperature of 1200c. In such procedure, the hexavalent chromium can be reduced to  $\text{Cr}^{+3}$ . A small experiment using this method has been done, and the result is encouraging. However, it is impossible to consume the huge stack of ore residue in a short time. Around the time that this procedure was recommended, a reduction method also was suggested. After the reduction treatment, the ore residue can be used to make bricks. The experiment using the reduction method indicates that water soluble hexavalent chromium was reduced to 0.045% of the total chromium contained in the ore residue from 30.98% before reduction treatment. However, the use of this kind of bricks is limited. Due to the same reason as the first method, it is infeasible to solve the contamination problem in a short time by using this method.

In November 1982, the alloy cooperation finished constructing the underground seepage prevention walls in order to isolate the contaminated solid waste. Total cost of the seepage prevention project was 4,210,000 Yen (approximately \$700,000). The seepage prevention wall was made out of cement. It was built to surround the stack of ore residue and had a total perimeter 800m, with a thickness of 0.7m. Average depth below ground surface was 14.45m. The isolated area was 10700m<sup>2</sup>. The average depth that the wall was inlaid into the decayed bedrock was 1.1m. The wall and the bedrock formed a huge container, which isolated the contaminated solid waste.(Figure 5 and Figure 6) Continuous monitoring in the following two years showed a significant effect of the seepage prevention walls on preventing underground water continuously being polluted.(Table 4) Because the underground water under the stack of ore residue was isolated, hexavalent chromium concentration outside the prevention wall dropped quickly. In Observing Well #14, built in 1982 inside the prevention wall, the hexavalent chromium concentration was 189mg/L in 1982; and the average hexavalent chromium concentration was 453.85mg/L (699.57-175.03mg/L) in 1983. In Observing Well #3, built in 1983, the hexavalent chromium concentration reached 282mg/L in 1984, compared to the absence

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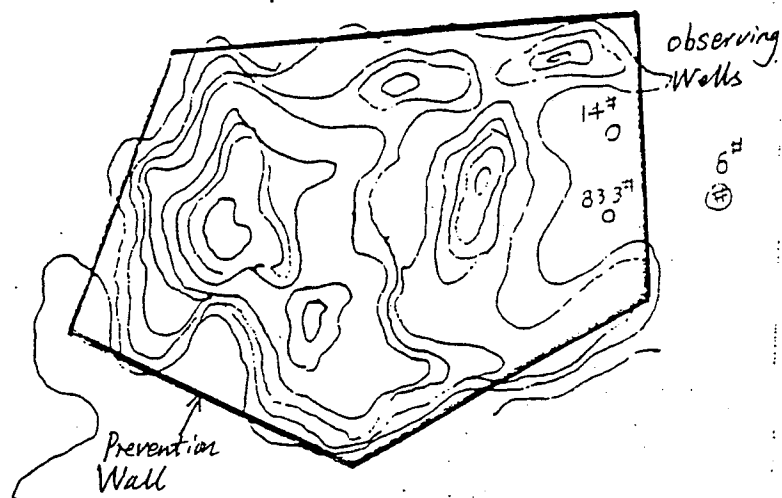


Figure 5: Diagram of Seepage Prevention

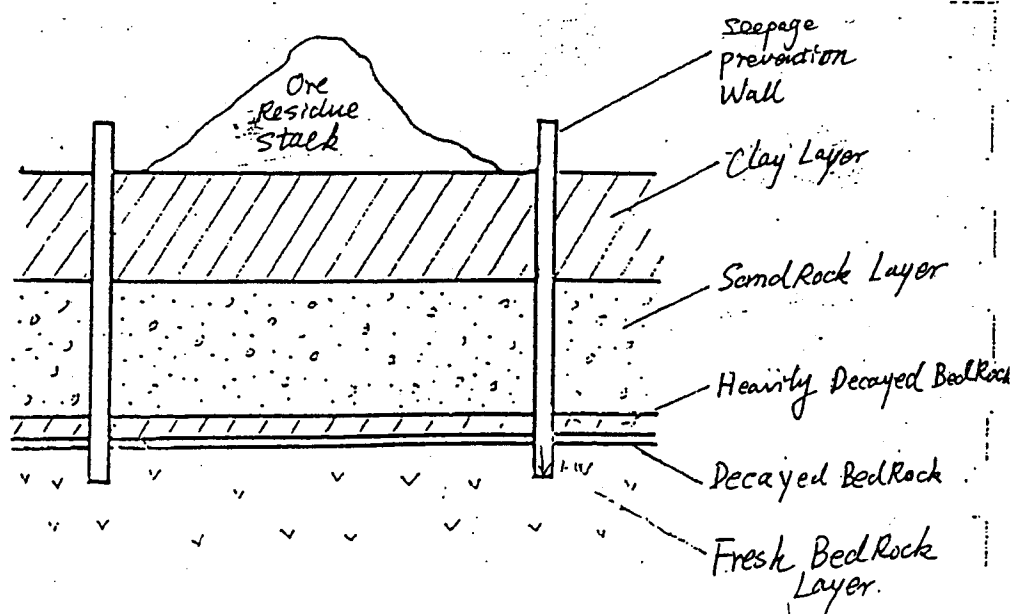


Figure 6: Cross Section Diagram of Seepage Prevention

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of a hexavalent chromium concentration in 1983.

Table 4: Hexavalent chromium concentration in the observing well #6  
(outside the prevention wall) (mg/L)

year	yearly average	yearly max	yearly min
81	18.15	38.22	7.47
82	14.46	28.32	5.05
83	4.30	8.65	2.01

After the prevention wall was built, the hexavalent chromium concentration of underground water in the contamination area gradually dropped.(Table 5) Compare 1983 with 1982, the hexavalent chromium concentration dropped at a yearly average of 26-33%; and the number of places exceeding hexavalent chromium concentration standard dropped 20-40%. This data indicates the seepage prevention wall was effective in isolating contaminated groundwater and preventing continuing hexavalent chromium spread. This result brings us to a new era in 20 years of treating the contamination. However, the average hexavalent chromium concentration in the soil one meter outside the prevention wall was still 407mg/Kg, which indicates it needs a longer time to clean the hexavalent chromium contamination thoroughly. The effectiveness of the prevention wall needs a longer time to evaluate. So thoroughly cleaning up of the  $\text{Cr}^{+6}$  contaminated underground water needs a longer time.

Table 5: Comparison of hexavalent chromium concentration (mg/L)  
in Underground water between 1982 and 1983 in the contaminated area

year	JinChangBao			Nuer River			WenJiaTun		
	A.S.	max	average	A.S.	max	average	A.S.	max	average
82	69.73	1.85	0.196	99.03	1.91	0.94	29.88	0.11	0.39
83	55.37	1.43	0.136	85.23	1.70	0.73	17.43	0.08	0.026

\* A.S. : above standard (%).

### Summary:

Now it is helpful to summarize the experience of treating this hexavalent chromium contamination in the past 20 years. It is still not clear what the effect of this contamination is on human health and on environment. As shown in this paper, the processes of this contamination were the following:

1. Underground water was contaminated with hexavalent chromium
2. Hexavalent chromium accumulated in soil and changed the function of soil
3. Contaminated soil had lower productivity, which caused crops production reduced.
4. Crops with high hexavalent chromium density affected human health.

This process still needs more study. The questions we have now are the following

1. What is the procedure of pollutant transferred from underground water and soil?
2. What is the effect of treatments to the contamination?
3. What is the effect of hexavalent chromium contamination to soil, crops, human health?
4. What is the long term effect of this contamination?
5. What is sensible measure to evaluate contamination like this?

The seepage prevention wall cannot be considered as a final solution. It needs a longer time to evaluate the effectiveness of this method.

### **Reference**

- (1) *Annual Reports of JinZhou Health and Anti-epidemic Station*
- (2) *The report of the Hexavalent chromium Contamination by Discharged Sewage from JinZhou Alloy Cooperation. (JinZhou Health and Anti-epidemic Station, 1979)*
- (3) *The report of investigation of underground water and contamination (JinZhou Environment Monitoring Station, 1985)*
- (4) *Evaluation of Condition of JinZhou drinking water. (Zhang Guo Kuang, 1984)*
- (5) *Report of the investigation of the vegetables growing in contamination area. ( Wang Gui Shen, 1983)*
- (6) *Study of the Malignant Tumor Cases in JinZhou Suburb. (Zhang Jian Dong et al, 1979)*
- (7) *Hexavalent chromium Effect in Deformity of Rates Chromosome. (Zhang Jian Dong et. al., 1980)*
- (8) *Possibility research of making mixed cement using ore residue containing hexavalent chromium. (Li Yun Jiang et. al. )*

Original Paper in Chinese was received on June 9, 1995.

Translation was finished on June 12, 1995 by Tony Ye

Electronic File is: a:trans.612

### *Comments of the translator:*

(1) The following names have been used as names of village and locations. In this translation, all the English names are Chinese Spelling Representation of the corresponding Chinese names. They are

JinChangBao, JinZhou, Nanshan, Nuer village, old Nuer River, Nuer River, SanDaoHao, ShiLiTai, WenJiaTun.

Do not confuse old Nuer River with Nuer River.

(2) To avoid communication errors, in the whole process of translation of this paper, we tried to use as much as possible the same words in English as the Chinese words used in the original paper. Because of that, sometimes we had to simplify some English grammar.

(3) For any different translation between this paper and the paper of "Chromium Pollution of Soil and Water in JinZhou", the translator used the corresponding English words as the original paper.

(4) There are two "Figure 2"s in this paper. According to the sequence of appearance and meaning in the paper, the translator used Figure 2A and Figure 2B.

(5) On page 5, the fourth paragraph is confusing. Even reading it in Chinese, the translator can not understand the meaning of the original paper. The translator recommended that the author be questioned about the meaning of this paragraph.

(6) In the original paper, there is a contradiction:

On page 3, "By the end of 1965..... the total contamination area was 20 km<sup>2</sup>."  
On page 4, "By 1974, the contamination area reached 45 Li<sup>2</sup> (11.25 km<sup>2</sup>)."

It is not consistent with the expanding trend of the contamination mentioned in the paper. Translator thinks that there is a printing error in the original paper. In fact, there is only a slight difference between Li<sup>2</sup> and Km<sup>2</sup> written in Chinese.



(7) This is the paper which summarized the Chromium Contamination from 1965 to 1985. Several studies of the effect of the contamination on human health were mentioned in this paper. In the list of reference, we can find one of them (reference number 6). Apparently, it will be very helpful to get more detailed reports on these studies to understand the effect of chromium contamination on human health.

(8) This paper was published in 1986. I think they have the data of monitoring this contamination after 1986. At least, they may include reports of the current condition of this contamination in the Annual Report of the Health and Anti-Epidemic Station. These reports are very useful. In this paper, the author put in the following statement:

" It needs a longer time to evaluate the effectiveness of the seepage prevention wall....."

" The effect of the contamination on human health is still an open question."

Further monitoring data or reports are helpful in answering these questions.

(9) Any question, please call Tony Ye @ 510-748-5675



# 锦州的铬污染事件

张建东 李希林

(锦州市卫生防疫站)

## 一、前言

1965年1月26日，锦州市郊区（现在和区）女儿河、金厂堡两屯一些水井的水变黄，群众要求查明原因。锦州市卫生防疫站当即组织现场调查并证实：部分居民水井水所变黄，做饭呈绿色，不能饮用。据悉水质改变已有半年左右，由于近期颜色加重才引起人们的疑虑。现场调查确认

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地下水遭到六价铬(略 $\text{Cr}^{+6}$ ,下同)的严重污染。此后近二十多年来有关方面对污染的原因、污染程度、污染对环境及人体健康的影响和污染的治理进行了大量的调查监测工作。到目前为止已经清楚了整个污染事件的发生、发展过程。

这起 $\text{Cr}^{+6}$ 对环境的污染事件,其污染范围之大,危害程度之深远,持续时间之长,均为国内外所罕见。在二十多年里,有关方面在调查、监测、治理工作中积累了大量宝贵材料,在工作中也得到诸多失败与成功的教训;现在已有条件对整个污染事件进行较全面的总结,来汲取有益的经验,并进一步就污染事件的未来研究方向和课题进行讨论。

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## 二、污染源

$\text{Cr}^{+6}$  污染的来源在于该地区的有色金属冶炼厂——锦州铁合金厂。该厂建于40年代，1959年开始研究试炼金厚铬，61年小规模投入生产，当时的回收率只有24.5%，63年提高到56.3%，以后数年回收率一直在60%左右，致使大量铬盐流失。65年开始大批量生产，金 $\text{Cr}^{+6}$ 废水剧增，每小时最大排出量为125吨，浸出废水中 $\text{Cr}^{+6}$ 最大浓度为105 mg/L，沉淀处理前废水中 $\text{Cr}^{+6}$ 浓度也为79 mg/L，污水排出口（厂东门）处，污水中含 $\text{Cr}^{+6}$ 浓度仍呈20 mg/L左右。废水全部排至厂外明沟。

生产过程中的焙烧、浸出等工序，又使大量含铬废气向大气中扩散。

生产废渣约1500多吨均散放在厂内外  
的空地之上。由于生产管理不严，生产设  
备的跑、冒、滴、漏竟达30多处。

所以，经五年多的长期积累，及该地  
的特殊地理环境，终于酿成一起以 $Cr^{+6}$ 为  
主要污染物的既有气相，水相又有固相的  
复杂而持久的污染事件。在这一污染中又  
以地下水被污染为主要表现形式。

铁合金厂所立地的水文地质特征是耕  
地这一污染的因素之一。 $Cr^{+6}$ 污染带分布  
在女儿河北岸的漫滩阶地，为低山丘陵后，  
基岩风化较重，岩石破碎，裂隙发育，地  
势较高，处于地下水补给区。地下水埋深  
1—4米，含水层为砂砾石混粘性土，厚  
3—7米，水量丰富；地下水流向东南。

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地层土壤渗透系数  $K=150-200$  米/日, 地下水流速  $0.162$  米/小时。

含  $Cr^{+6}$  污水除部分由车间地面及厂内集水池渗入地下外, 大部自厂东门排水口进入地面明沟, 流向东南。在厂堡东北汇入女儿河古河道(见图1), 古河道是一干涸河道, 已改为铁合金厂排水河道(即小八沟)。  $Cr^{+6}$  自车间、厂内及明沟排放道渗入地下, 是导致被  $Cr^{+6}$  污染的原因之二。

当污染出现以后, 该厂对散放至厂内的含  $Cr^{+6}$  废渣(浸出尾渣), 集中于厂南空地堆积, 一座“渣山”开始形成。渣山逐年扩大, 现已占地  $50$  亩。起初 ~~渣山~~ 在渣堆底部用毛石水泥铺底, 加洒青油毡

(13×15-370)

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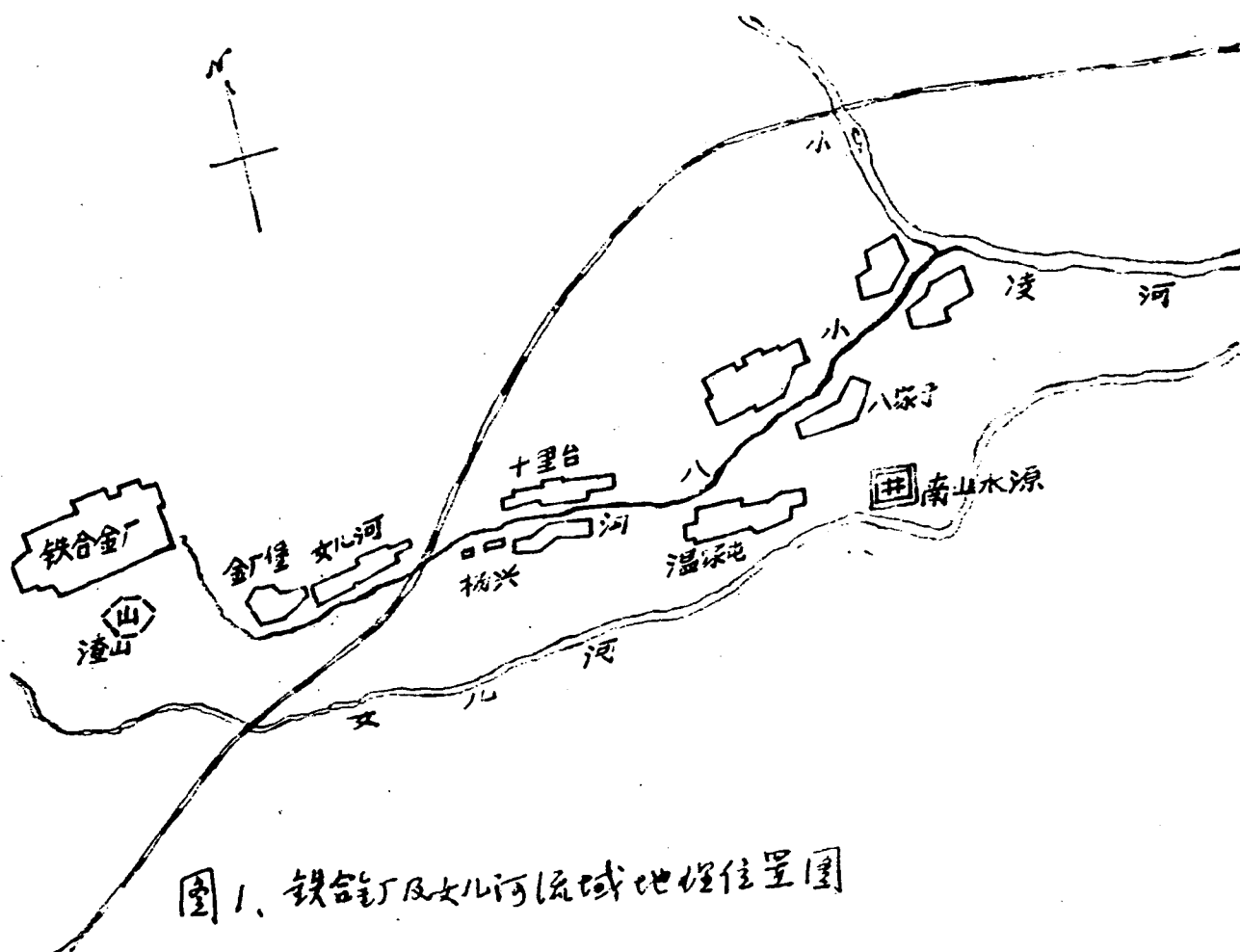


图1. 铁合金厂及女儿河流域地理位置图

(20×15=300)

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防渗，四周建围墙以防护。当废渣逐年增加，已由堆放初期的1500吨，到现在已达30万吨，故原建的渣场早已埋设在渣山的中心，过去的防渗处理已不起作用。因而，由于含 $Cr^{+6}$ 废渣长期露天堆放，雨水淋漓，风吹扩散，使 $Cr^{+6}$ 进入地下是造成该地地下水资源被 $Cr^{+6}$ 污染的主要原因之一。

### 三、污染的过程及危害

事件发生后的调查认为，地下水的污染系源于厂区及车间的渗漏。在长达20多年的污染过程中，污染的范围和强度，都在不断改变，废水、废渣对地下水污染所占的主导地位已有所更替。

本污染起始于1960年，到65年初，污

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染范围仅限于女儿河、金厂堡两屯的中间地段 (见图 2)

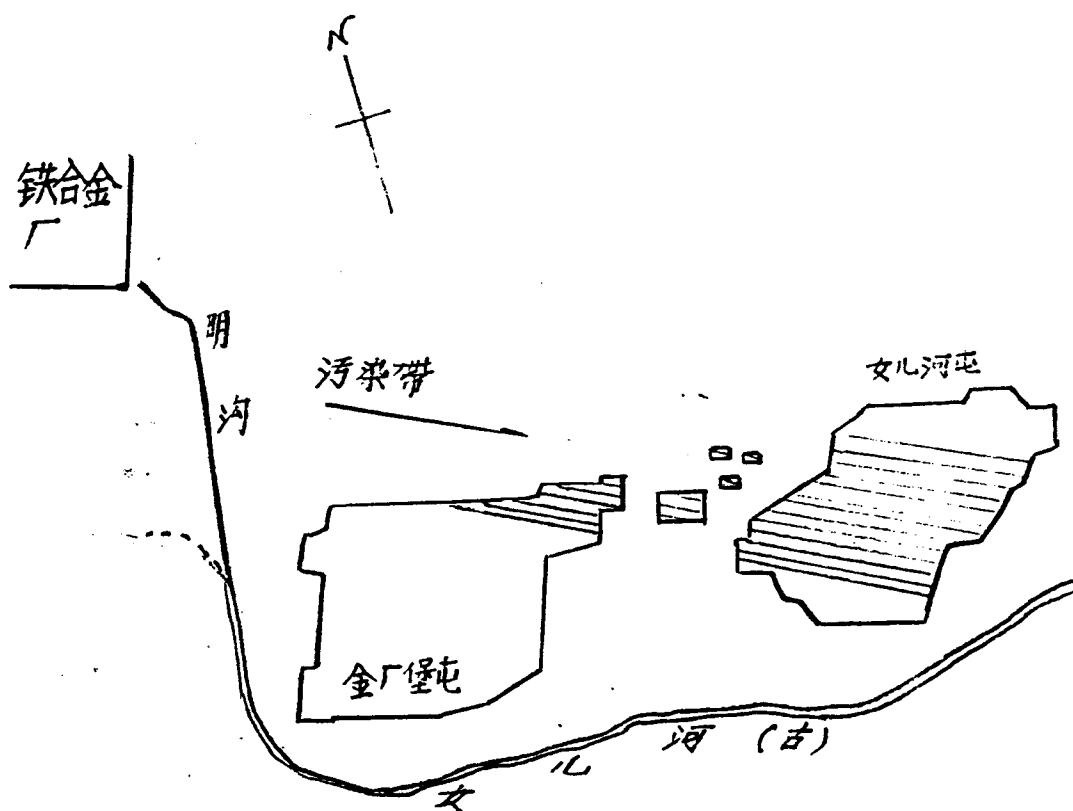


图 2. 1965 年金厂堡、女儿河屯  $\text{Cr}^{+6}$  污染范围示意

1965 年观测井的化验结果表明, 地下水的污染以铬生产车间为起点, 形成与地下水流向相一致的长带状污染带。这条带

(18×15—370)

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染带以车间渗漏和排污沟污水下渗为主得以形成。在地下呈槽状分布， $\text{Cr}^{+6}$  浓度在槽的断面中间含量增高，两侧偏低，与地下水的高度呈相反的趋势。因而地下水的梯度限制了  $\text{Cr}^{+6}$  在地下水体的横向扩散，遂形成带状污染带。而首先受到影响的则是女儿河屯。

65年初，女儿河、金厂堡屯共有水井266眼，有  $\text{Cr}^{+6}$  检出的75眼（占28.2%），最高检出值为  $10 \text{ mg/L}$ ，最低为  $0.6 \text{ mg/L}$ ，其中有41眼井（54.67%）检出值在  $2.0 \text{ mg/L}$  以上。

65年后，地下水污染已扩展到金厂堡屯的一半（占全屯水井的40.65%），女儿河屯的大部分（占全屯水井的95.88%）有  $\text{Cr}^{+6}$  检出。并已扩展到下游的女儿河车站，

(18×15=270)

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杨兴屯，十里台，温家屯，八家子等地段。

污染区域达20平方公里。在上述村屯的144眼水井的调查中，有92眼（63.88%）检出 $\text{Cr}^{+6}$ ，其中女儿河串站，杨兴屯最高检出值达 $5.0 \text{ mg/L}$ ，其它村屯都在 $0.05 \text{ mg/L}$ 以下。

造成下游地区污染的原因，除上述污染带向下扩散外，古河道（小八沟）内 $\text{Cr}^{+6}$ 河水的下渗是一主要因素。古河道自女儿河屯以下，因砂层裸露，全部污水至杨兴屯以西，已全部下渗，河道仍旧干涸。

严重的是，66年距污染源约18华里的锦州市南山水源，已有 $\text{Cr}^{+6}$ 检出，浓度在 $0.001 \sim 0.002 \text{ mg/L}$ 之间。

南山水源的主要补给水为女儿河，由于地势的原因，杜尔宝节时古河道流域的地下水发生对女儿河的补给，所以在女儿河水中也有  $\text{Cr}^{+6}$  检出；66年5月曾高达  $0.07 \text{ mg/L}$ ，此时南山水源水中  $\text{Cr}^{+6}$  达  $0.002 - 0.003 \text{ mg/L}$ 。69年水源水中  $\text{Cr}^{+6}$  含量在  $0.002 - 0.004 \text{ mg/L}$  之间。

1974年，受污染的面积已达45平方公里，污染源已沿古旧河道周围形成一狭长的污染带，并逐渐向四周扩散。金厂堡、女儿河地方地下水  $\text{Cr}^{+6}$  含量已增高到  $70.5 \text{ mg/L}$ ，较远的十里台、温家屯，地下水  $\text{Cr}^{+6}$  也达  $0.05 - 0.01 \text{ mg/L}$ 。

1979年，在几年来采取一系列处理措施之后，铁合金厂排河口附近  $\text{Cr}^{+6}$  浓度已下降，

金厂堡、女儿河一带地

下水  $\text{Cr}^{+6}$  在 4.33—0.06 mg/L 之间，杨兴、十里台一带也在 0.03—0.001 mg/L 间，新扩散的其它地区仍有 0.014 mg/L 的检出，女儿河水中  $\text{Cr}^{+6}$  含量在 0.99—0.167 mg/L 间。79 年是立整污染地区的最远距出上地下水  $\text{Cr}^{+6}$  含量出现最大和较大值的一年（见表 1）在 79 年前总的趋势是污染强度逐年增高，污染范围逐年扩大。而 79 年后，则开始出现降低趋势。

通过多年的调查实践证明，含  $\text{Cr}^{+6}$  废水的排放是本污染事件起始原因，而得以持续长期的扩大污染则由因含  $\text{Cr}^{+6}$  废液的堆积。因此立二十多年的污染过程中逐渐呈现出其固有的规律：

1. 含  $\text{Cr}^{+6}$  废水一般是以较均匀一致地流量外排流入地面，或渗入地下。由于污染被发

表 1 污染区内不同地段地下水  $\text{Cr}^{+6}$  含量年变化 (mg/L)

地区	金厂堡 女儿河	十里台 相 兴	温家五 八泉水	西山水源	女儿河 河水
距污染源 km	1.5	3~3.5	5~5.5	7.5	1.5
1965 年	0.6—10.0				
1966 年		0.002—20.1		0.001—0.003	0.07
1969 年				0.002—0.004	
1974 年	70.5	0.01—0.05			
1976 年				0.002—0.004	
1979 年	0.06—7.33	0.001—0.03	0.003 —0.004	痕量 —0.014	0.167—0.17

(20 × 15 = 300)

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现以后，工厂采取积极的治理措施，外排废水中 $\text{Cr}^{+6}$ 很快下降。1966年废水中 $\text{Cr}^{+6}$ 含量已开始降至 $3\text{mg/l}$ ，虽然各年中也曾有过较大的波动，但废水的污染在66年后，已成为小量的持续性的由地面流过并渗入地下。

2. 对比之下，在长期的污染过程中起主导作用的是“渣山”对土壤和地下水的污染。

渣山现有铬渣30万吨，新渣 $\text{Cr}^{+6}$ 平均含量为1.55%，久存渣为0.34%。受雨水淋溶，使 $\text{Cr}^{+6}$ 在土壤中富集，并迁移至含水层中。在渣场下的土层中 $\text{Cr}^{+6}$ 最高富集含量出现在1m以上的粘土层中。由于渗透性不好，结耕致密，土壤中 $\text{Cr}^{+6}$ 含量最高达 $4700\text{mg/kg}$ 。向下则为小块结耕，渗透性好，大气降水直接渗透到含水层，所以 $\text{Cr}^{+6}$ 含量降低。用地下水动储量的

方法估计, 渣山每天向地下水中转移约 0.3 吨左右的  $\text{Cr}^{+6}$ , 可见其污染容量之大。

3. 由于污染带形成的主要原因是渣山, 因而在污染带内不同井位的地下水污染浓度与渣山的距离呈线性关系。根据计算得回归方程:

$$\log \bar{C} = 1.6065 - 3.4486 \times 10^{-4}x$$

$$\bar{C} = 40.46 e^{-7.94 \times 10^{-4}x}$$

经检验与显著相关。  $|r| > |r_{\alpha}|$ 。充分说

明广大范围内污染带的形成, 是由渣山中  $\text{Cr}^{+6}$  对地下水的污染而引起并得以长期造成影响。

4. 渣山  $\text{Cr}^{+6}$  对地下水的污染程度, 直接取决于大气降水和当地的地质条件。在渣山周围地下水中  $\text{Cr}^{+6}$  一年内的浓度变



化中看出(图2), 丰水期 $Cr^{+6}$ 含量增高; 而在较远地区的地下水 $Cr^{+6}$ 浓度又是枯水期高于丰水期。充分说明, 丰水期虽然降水量大, 但

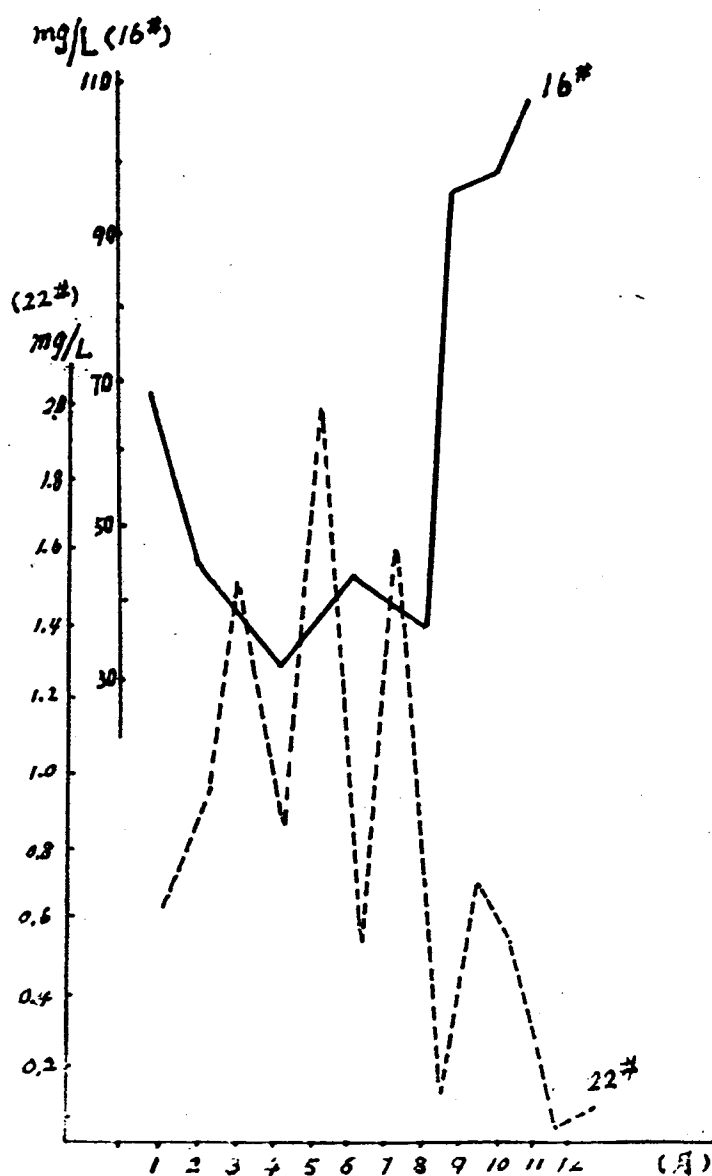


图2. 渣山下(16#)与较远地区(22#)地下水各月 $Cr^{+6}$ 浓度变化(1979年)

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因地下水位较高，补给及开采量都很大，导致流速加快，污染物很快运移，污染范围很快扩大。相反，枯水期地下水开采量减少，污染物运移缓慢；这是锦州地下水受  $Cr^{+6}$  污染的一个特点。

所以在锦凌山不断大量堆积的条件下， $Cr^{+6}$  污染事件必然得以长期的持续，污染强度和污染范围都在不断的加强和扩大（见图3）。只是在80-82年间对锦凌山应用混凝土防渗墙控制污染的措施后，地下水  $Cr^{+6}$  污染情况才趋于缓和。

## （二）对农作物的影响和危害

在  $Cr^{+6}$  污染的广大地面上，是锦州市的主要蔬菜产区，菜田用水来自污染带内的大量灌溉井。灌溉井水中  $Cr^{+6}$  含量均较高，平均浓度

(20 × 15 = 300)

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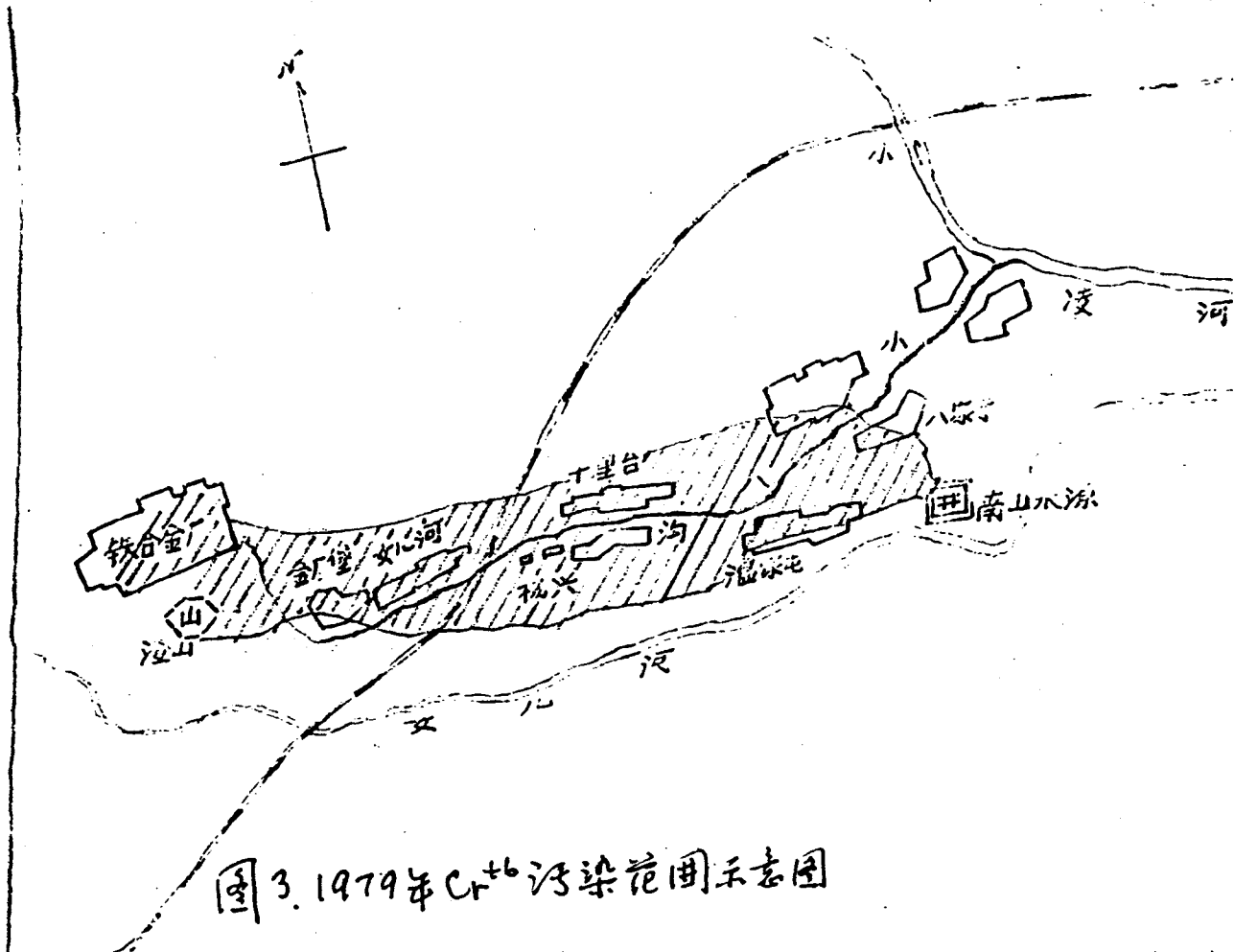


图3. 1979年 $Cr^{+6}$ 污染范围示意图

(20 × 15 = 300)  
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在  $0.006 - 0.739 \text{ mg/L}$  之间，灌溉面积达 1800 亩左右。由含  $\text{Cr}^{+6}$  的地下水长期灌溉，致使  $\text{Cr}^{+6}$  在地表土壤中逐渐积累。据 82-83 年调查灌溉的土壤中  $\text{Cr}^{+6}$  含量在  $62.5 - 67.5 \text{ mg/kg}$ ，而未受  $\text{Cr}^{+6}$  污染的地下水灌溉的土壤  $\text{Cr}^{+6}$  本底值仅在  $59.5 - 61.5 \text{ mg/kg}$ 。说明由于较高浓度地下水 ( $\text{Cr}^{+6}$ ) 以灌溉的形式输入菜田，使土壤中出现  $\text{Cr}^{+6}$  的积累；因而必然对该种植的蔬菜产生一定的生物学效应。据调查在  $\text{Cr}^{+6}$  污染带内蔬菜  $\text{Cr}^{+6}$  含量较对照区显著高 (见表 2)

表 2. 铬灌区与清灌区蔬菜  $\text{Cr}^{+6}$  含量比较 ( $\text{mg/kg} \cdot \text{鲜}$ )

	铬灌区	清灌区	t 检验
大白菜 ( $\bar{x} \pm s$ )	$0.025 \pm 0.015$	$0.011 \pm 0.001$	$p < 0.05$
甘 兰 ( $\bar{x} \pm s$ )	$0.014 \pm 0.0056$	$0.007 \pm 0.0025$	$p < 0.05$

在不同浓度的含  $\text{Cr}^{+6}$  地下水灌溉同一品种蔬菜体内  $\text{Cr}^{+6}$  含量也与灌溉水  $\text{Cr}^{+6}$  浓度呈正相关 (表 3)。

表 3.  $\text{Cr}^{+6}$  灌区不同浓度地下水与白菜  $\text{Cr}^{+6}$  含量比较 (鲜)

地下水 $\text{Cr}^{+6}$ 浓度 (mg/L)	白菜 $\text{Cr}^{+6}$ 含量 (mg/kg)
0.006	0.024
0.008	0.030
0.100	0.015
0.330	0.039
0.540	0.041
0.700	0.059

$$\hat{y} = 0.0463x + 0.0217 \quad r = 0.8844$$

外来  $\text{Cr}^{+6}$  在菜体内的分配也不均衡, 其中以根部负荷最多, 茎叶次之, 果实甚少。但是在盆栽试验中表明,  $\text{Cr}^{+6}$  水灌溉后, 作物的生长、发育、光合 ~~效率~~ 生物量, 都受到极大影响, 其必然是事实上许多蔬菜产区作物减产的重要原因。致于高浓度含  $\text{Cr}^{+6}$  的蔬菜对人体健康

(20×15=300)  
(59126, 8412)

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的危险，尚待进一步观察。

### (三) 污染对人体健康的危害

污染事件发生之初，由于以含  $Cr^{+6}$  废水直接污染地下水，人群直接饮用  $Cr^{+6}$  浓度严重超标的生活用水，在 1965 年于局部地区（女儿河、金厂堡屯）群众已有腹泻、腹痛、烂嘴角等症状出现。其后陆续在距污染源较远的地方也相继出现类似症状发生的人群，直至 1974 年在最远的地方（温家屯）也出现轻微反应。

长期饮用高浓度  $Cr^{+6}$  的生活用水，可以在人体引起胃肠道系统疾患增加，国内外都有类似的报告。而在本次污染事件中，据 1965 年对女儿河村 155 人调查，有口角糜烂者 51 例（33%），腹泻者 26 例（17%），腹痛 48 例（31%），消化不良 26 例（17%），心口痛 31 例（20%），呕吐

(20×15=300)

[59126.8412]

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20例(13%)。对高污染区居民12例末梢血粒粒中发现白细胞计数偏高( $5100-16300/\text{mm}^3$ )。在93例末梢血中又发现中性粒细胞中幼稚型细胞数偏高,呈有核左移倾向。当时饮用水中 $\text{Cr}^{+6}$ 浓度在 $0.1-20.0 \text{ mg/L}$ 。上述反应呈一过性发作,当饮水条件改善,或机体对环境适应时即告消失。

1971年,十里台也出现上述症状,据对158人调查发现,口角糜烂者92例(58%)腹痛48例(30%)腹痛36例(23%)消化不良16例(10%),与1965年女儿河发病的症状相似,所不同的是该地下水中 $\text{Cr}^{+6}$ 浓度仅在 $0.003-0.05 \text{ mg/L}$ 间,而水中硫酸盐浓度已大于 $300 \text{ mg/L}$ ,最高达 $700 \text{ mg/L}$ 。1974年五里原区、三道岭部亦出现类似情况。提示了已混有硫酸盐污染水道

(20×15=300)

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成人群危害的迹象。

据 1970—1978 年对污染带地区人群死因回顾调查资料中看出，处于污染带上的金厂堡、女儿河、十里台、杨兴、温家屯的居民恶性肿瘤死亡率在 73.42—99.30/十万（调整死亡率在 71.88—92.66/十万）之间，而同时期锦州市太和区恶性肿瘤平均死亡率仅为 65.40/十万。其中肺癌死亡率在 13.17—21.39/十万（同时期全区平均为 11.21/十万）胃癌死亡率为 27.68—55.17/十万，也高于全区平均水平，成为当时太和区恶性肿瘤高发的地区。且有越靠近污染源，恶性肿瘤死亡率越高的迹象。这不能不认为与地下水、土壤及农作物受  $\text{Cr}^{+6}$  的污染存在着某种间接的联系。立时  $\text{Cr}^{+6}$  诱发小白鼠骨髓细胞染色体畸变的实验结果

（1980 年）中也发现  $\text{Cr}^{+6}$  能引起小白鼠骨髓细胞

(20 × 15 = 300)

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胞染色体畸变率的增高，更加证明  $Cr^{+6}$  污染必然给人群健康带来上述诸多危害的可能。

#### 四、防治措施和人为污染的形成

1965 年发现污染后，人们注意到  $Cr^{+6}$  废水对地下水的严重污染，并经锦州市委决定于 66 年 4 月停止生产进行改造。当时采取的主要措施是：

(1) 改进焙烧。将原卧式焙烧、加热水浸改为球磨粉碎，冷却水浸；防止了  $Cr^{+6}$  蒸汽向大气扩散。

(2) 地面防渗。对厂内向地下渗透<sup>含</sup>高浓度  $Cr^{+6}$  液体（最高达 105 mg/g）的车间地面，做防水防渗处理。

(3) 将废水经废水处理站处理后集中排放。该站由厂内排水，设有人水管，雨前加

硫酸亚铁处理。

(4) 为确保  $\text{Cr}^{+6}$  不再排出厂外，在污水排放口前建沉淀池一座。在加入硫酸亚铁后，以石灰乳沉淀再行排出。

(5) 在地下水的污染带上，分别于厂东内，金厂堡北，女儿河北打三眼截流井，抽取地下水，加硫酸亚铁处理。对厂内地面表土也用硫酸亚铁渗入净化处理。

经上述处理，在67年后地下水  $\text{Cr}^{+6}$  浓度很快有所下降，并在多年中趋于稳定。南山水源（北付井）虽一度受到  $\text{Cr}^{+6}$  的污染，在多年来其浓度一直在痕迹量—— $0.004 \text{ mg/l}$  之间变动，没有出现大幅度的上升。

然而，由于当时所采取的各项措施中，

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主要以向含  $\text{Cr}^{+6}$  废水，及抽出的含  $\text{Cr}^{+6}$  地  
下水中大量倾注硫酸亚铁的措施，投加量  
不经计算，甚至往往采取将抽出的井水直  
接倾注在硫酸亚铁堆上，并任其流走。  
因而就造成这样的后果：（1）渣山的形  
成，含  $\text{Cr}^{+6}$  废水对地下水和土壤的长期、  
大量的持续污染。（2）硫酸盐对地下水  
的污染。即形成了新的人为的硫酸盐污染。  
这两种后果都应成为  $\text{Cr}^{+6}$  污染处理史上的  
深刻教训。同时，采用排水截流的方法，  
能较快的改善地下水的状况，控制  
污染物向下游稀释扩散，但当截水行泵时  
确实发现因行泵使排水中  $\text{Cr}^{+6}$  迅速降低的  
现象。充分说明截流排水的方法加快了地  
下水的流动，从而也加快了污染物的迁移，

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随着减压漏斗的形成和扩大，在难于长期排水的情况下，就不可能成为清除污染的可靠手段。

由于硫酸盐污染的形成，在南山水源的水质监测中观察到：1967年以来，水中硫酸盐、氯化物的含量逐年上升，水的硬度也急剧改变并不断增高，地下水的水质发生了不可逆转的恶性变化。65年水源水的硬度尚不足 $100\text{ mg/L}$ ，到80年已升至 $199.26\text{ mg/L}$ ，个别水井的最高值达到 $307.23\text{ mg/L}$ 。水源水的氯化物含量66年仅为 $20-22\text{ mg/L}$ ，到80年已超过 $70\text{ mg/L}$ ，

硫酸盐由 61 年的 20-30 mg/l, 上升到 80 年的 100 mg/l, 82 年又达 122.3 mg/l (见图 4)。在

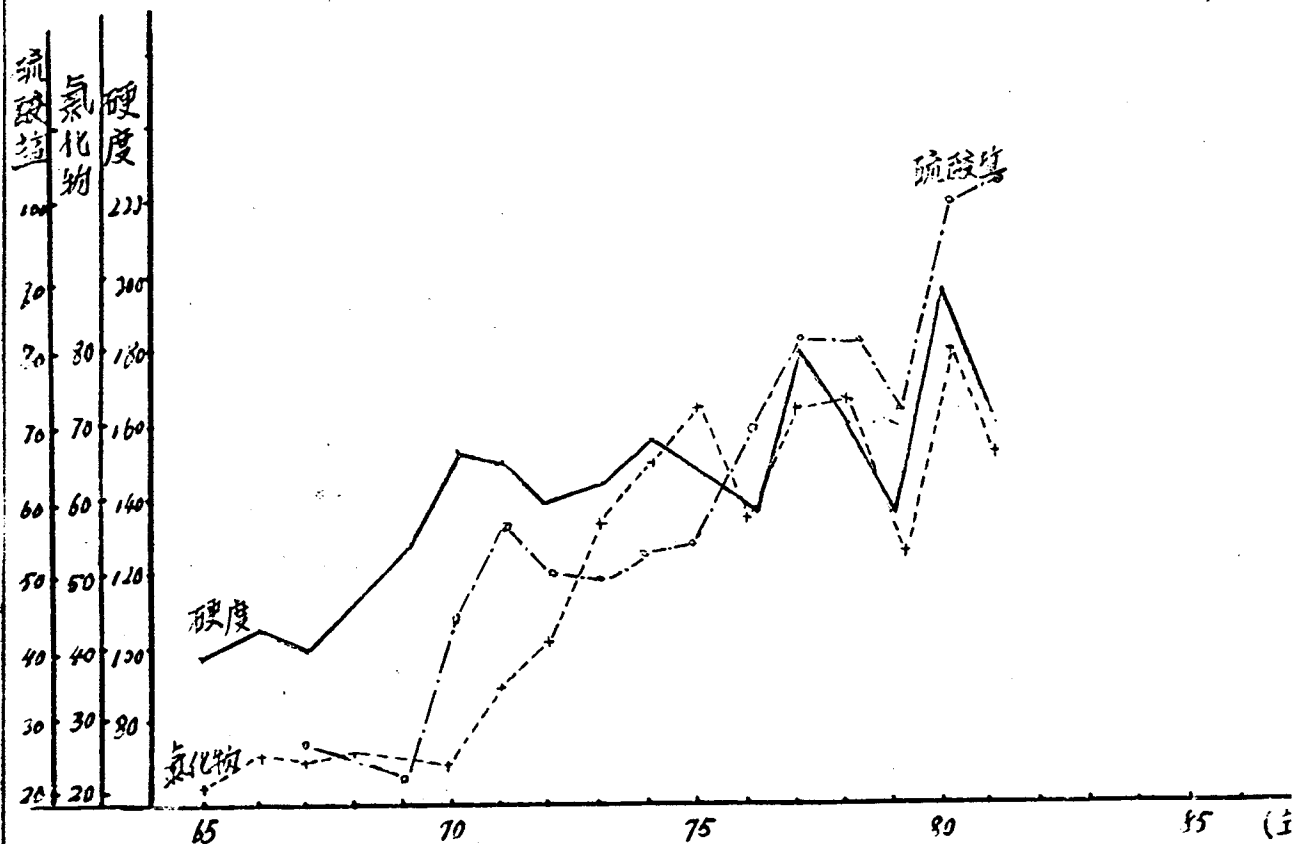


图4. 南山水源水质(硬度、氯化物、硫酸盐)各年变化趋势

沿辽河沿岸的井水中硫酸盐一般都达 250-300 mg/l 左右, 个别最高值(金厂堡)曾达到 830~966 mg/l 这使广大范围内的更多人身受其害。

## 五、渣山的治理及效果评价

渣山形成以后，逐年积累，不断增加，大量 $\text{Cr}^{+6}$ 随雨水淋溶进入地下，造成大面积的长期持续污染，已成为必须立即解决的课题。

截流地下水虽对牵制 $\text{Cr}^{+6}$ 的污染取得一定的效果，但经实践证明是一项得不偿失的措施，不能再继续进行。80年以后，曾有人提出用渣烧制水泥混合材料，通过高温（ $1200^{\circ}\text{C}$ 以上）加煤研石、硅酸铝等进行焙烧，使渣中 $\text{Cr}^{+6}$ 还原成 $\text{Cr}^{+3}$ 。虽进行了小型试验，取得了可喜的成绩。但由于渣量积存量过大，生产能力有限，仍不能从根本上解决渣山的污染。

与此同时，也曾有人提出用渣渣还原/固化、硫制硫酸。经试验证明，在烧制渣位以后，水溶性 $\text{Cr}^{+6}$ 已显著减少；由原 $\text{Cr}^{+6}$ 含量

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中总盐的 30.98% 下降至 0.045%，效果是非常显著的。但也因与生产渣砖的能力与渣山的堆积远不相适应，渣山仍然长期不能被吃掉。加之卫生院的渣砖仍在使用中又受到某些必要的限制，因而这一方案的实施仍受到很大限制。

1982 年，该厂开始修建渣砖地下帷幕，即地下混凝土防渗墙，以隔出  $C_{10}$  污染区——地下水，期望彻底控制污染。

地下帷幕混凝土防渗墙于 1982 年 11 月开工建成。工程总投资 421 万元。墙体以围绕渣山外围成一闭合体，周长 800 米，墙体宽 0.7 米，平均厚度为 1.45 米。墙体嵌入弱风化闪长岩平均 1.1 米。截水面积 1.07 万平方米。渣砖厂成为工厂内渣砖被封闭在地下岩层上的大型混凝土池中（见图 5.6）。

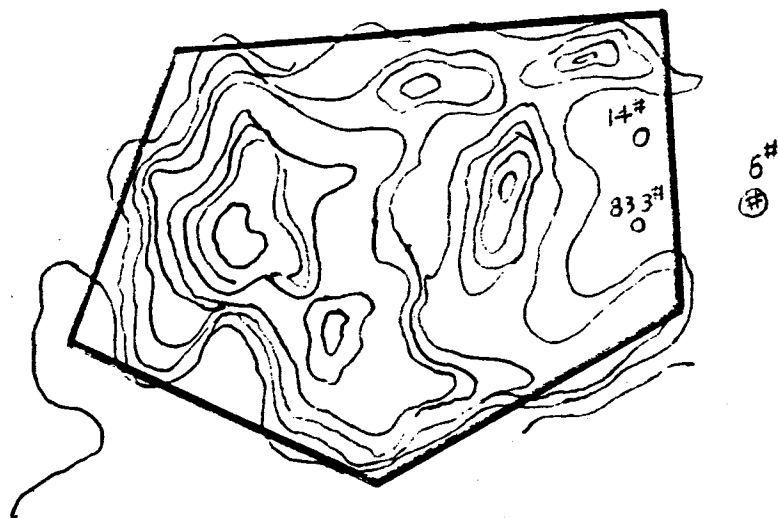


图5 渣山及防渗工程平面示意图

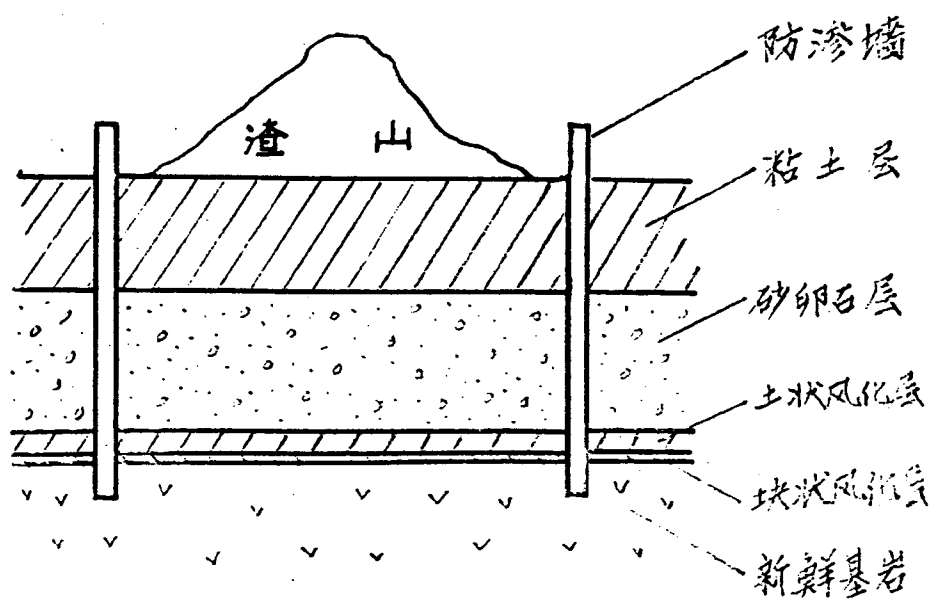


图6. 渣山及防渗工程剖面示意图

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经两年多的连续观察证明，防渗墙对制止地下水的继续污染，已收到显著效果。由于墙堆下地下水被完全阻断，在围墙建成以后，墙外地下水  $Cr^{+6}$  含量迅速下降（见表4）。

表4 墙外(6#)井水  $Cr^{+6}$  含量变化 (mg/L)

年	年平均	最高值	最低值
81年	18.15	39.22	7.47
82年	14.46	28.32	5.05
83年	4.30	8.65	2.01

在墙内，于82年10月建成的14#观测井中，当时  $Cr^{+6}$  含量为  $189 \text{ mg/L}$ ，83年年平均达  $453.85$  ( $699.57—175.03 \text{ mg/L}$ )。83年建成的83-3#观测井在一年多的连续观测中， $Cr^{+6}$  含量由不能检出逐渐上升到  $232 \text{ mg/L}$ 。

防渗墙建成后，在污染地区的不同地段地

下水  $\text{Cr}^{+6}$  含量也逐年下降 (表 5)。

表 5. 82-83 年污染地区地下水  $\text{Cr}^{+6}$  含量比较 (mg/L)

年	金 厂 堡			女 儿 河			温 家 屯		
	超标 %	最高 值	平均 值	超标 %	最高 值	平均 值	超标 %	最高 值	平均 值
82 年	67.73	1.85	0.196	99.03	1.91	0.94	29.58	0.11	0.39
83 年	55.37	1.43	0.136	85.23	1.70	0.73	17.43	0.08	0.026

两年相比较, 年平均值下降 26-33%, 超标率普遍减少 20-40%。已充分证明地下帷幕混凝土防渗墙在阻断地下水, 防止  $\text{Cr}^{+6}$  的持续污染, 从根本上治理路渣的危害方面, 已收到了可靠的效果。持续了二十多年的路污染已开始进入逐步清除的新时期。但由于墙外地下残存污染物质, 每年仍造成墙外地下一米小土堆平均  $\text{Cr}^{+6}$  含量在 40 mg/kg 左右, 况且防

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污染源本身尚须经过较长时间的验证和认证，因此地下水彻底消除 $\text{Cr}^{+6}$ 的污染仍需要相当长的时间。

## 六、存在的问题（小塔）

回顾二十多年锦州路污染的历史，总结其污染过程、治理过程中的经验和教训是有意义的。

人类的认识过程就是在不断的探索，并在大量的历史事实面前不断得到验证的过程。

迄今为止为止，仍不能认为这一污染事件对环境 and 人群健康所造成的危害是清楚的。当前的

问题是，通过地下水污染以后， $\text{Cr}^{+6}$ 在土壤中逐步富集，并得到与土壤的组成、结构和功能

的变化，从而影响植物的正常生长发育，以致使作物产量和质量下降，最终影响人群健康。

这样一个已在事实上存在的土壤污染，仍是

研究得很深入的课题。污染物在地下水和土壤中的迁移、转化过程究竟怎样，污染物在迁移过程中还会有些什么规律和什么样的情况，在长期的污染过程中， $\text{Cr}^{+6}$ 对土壤、对农作物、对人群健康的危害，及其远期效应究竟如何或者用什么样的更敏感的指标去观察和评价，这都有待进一步的研究、讨论。在目前，地下帷幕混泥土防渗墙的建成，还远不能认为是最终治理污染的有力措施，其远期防污效应都亟需进一步的监测研究和长期的历史验证。

1986年2月。

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