Management and Treatment of Wastewater in Hunan's Nonferrous Mines in China

By XIE LONGSHUI,[2] ZHAO CHUNBAO[1] and ZHANG ZHENCHUAN[2]

Changsha Institute of Mining Research, Changsha, Hunan, China

Hunan Agency of Environmental Protection, Changsha, Hunan, China

ABSTRACT

As known to the international mining sectors, Hunan province, called as ' Nonferrous Native Area ', is the main base of nonferrous metals production in China. There are over 194 nonferrous mines in this province, most of them distribute over the basin of Xiangjiang River. The state of management of wastewater in Hunan's nonferrous mines is outlined. The experiences and economic benefit in the management and treatment of wastewater in Bofang and Mayang copper mines, and at Shizhuyuan polymetallic mine, are mainly introduced. It concludes with measures and recommendations for future management and treatment of wastewater in Hunan's nonferrous mines.

INTRODUCTION

Water is the source of life, and the most essential environment condition of the human living/life and the social development. Much waste water has been produced, because of mining. The discharge of wastewater pollutes the natural waterways, effects the self-purification capacity, degrades the environmental quality, but directly influences the human health, the ecological equilibrium, the zootope and the plant growth etc.. Therefore, the people have paid close attention to the influence of wastewater from the nonferrous mines on the environment. In order to protect the natural environment, bring the benefits to mankind and provide the good conditions for the animal living and plant growth, the sectors concerned have taken many suitable measures to protect water resources.

The examples and measures of wastewater management in Hunan's nonferrous mines in China are discussed in this paper.

QUALITY AND POLLUTING STRENGTH OF MINE WASTEWATER

Hunan province situated in South-Central China, at the middle reaches

*1 --- Senior Engineer; *2 --- Engineer

of Changjiang River and the North of Nanling Mountain. The rivers distribute all over the province. With the exception of the plain rivers of Dongting Lake, there are over 5000 rivers, which most of them belong to the water system of Dongting Lake, with more than 5 Km in length. Hunan, climatically, is temperate rainy region; notable in geographic environment, it is characteristic of so called ' Qishan Yishui Erfentian ', which means 70% is mountains, 10% rivers and 20% agricultural land.

Called as ' Nonferrous Native Area ', Hunan is the main base of nonferrous metal production in China. There are over 194 nonferrous mines in this province, most of them distribute over the basin of Xiangjiang River. As viewed from Hunan's natural conditions and the geographic position of mines, the mine wastewater is very apt to flow into and pollute the natural waterways. Operated by the county governments in Chenchou Region, more than 20 nonferrous mines distribute over the upper reaches of branches (Ex. Laishui, Chonglingshui, Yonglejiang etc.) of Xiangjiang River. The discharge of wastewater from these mines is up to 20 million tons per year. Currently, it is very serious that the rivers and lakes are polluted by the mine wastewater. For instance, the content of zinc element in the wastewater from both Longxia tailing reservoir and Huangshaping underground lead-zinc mine is respectively1.53 and 11.13 times higher than the normal value of wastewater discharge set forth in China, while the maximum detected value is 18 times. Relatively, it is more serious that the metal elements are overcontained in the wastewater from Shuikoushan lead-zinc mine, that is to say, the contents of copper, sulphide, lead, cadmium and zinc elements are individually 166.6, 61.35, 6.67, 4.25 and 3.26 times higher than the normal value of wastewater discharge. On the whole, the discharge of industrial wastewater in Hunan province is up to 2000 million tons annually, in which the discharge of wastewater from the nonferrous mines into Xiangjiang River is more than 200 million tons per year.

The toxic elements in the mine wastewater are varied with the different kinds of orebodies. However, the toxic elements in the wastewater from the processing plants are changed with the variation of ore and processing technology. The noxious elements in wastewater from the nonferrous mines in Hunan are shown in Table 1 - 2. No tailing reservoirs have not yet been employed in some of processing plants in the nonferrous mines in Hunan nowadays so that the tailings and wastewater are directly discharged into the natural waterways. In this way, the river courses are deposited, the agricultural land is emerged and the content of heavy metal elements in the soil is increased (Table 3). The wastewater in some mines will not be well treated, so some wastewater directly flows into the underground waterways. For instance, the content of cadmium elements in water in Songbo section of Xiangjiang River is very high, corresponding to two times higher than that of the ground-level water standard set down in China, related to that the wastewater from Shuikou Shan lead-zinc mine is directly discharged into Xiangjiang River. With the development of nonferrous metals industry, the content of radioactive elements in the water of Xiangjiang River is gradually increased. The radiomaterial concentration in the water and the bottom soil of Xiangjiang River is shown in Table 4.

In view of the circumstances above, the strength that wastewater from the Hunan's nonferrous mines has polluted the natural environment is

higher, so it is very necessary to manage and treat the mine wastewater.

Table 1 Noxious Elements in Mine Wastewater (mg/l)

Noxious Elements	Mines				
	Lead-Zinc	Tungsten	Antimony	Copper	Gold
Pb	0.5-1	0.36			<0.5
Zn	2-90	0.2-6			0.1-0.25
Cd	0.1-5	0.14-0.9			<0.025
S^{2-}	2-10	4-5		5-10	0.1-0.3
F	5-10		7-10		
SS	1000-3000		1000-1500		100-500
Cu		0.1-1.68			<0.025
Sb			5-10		
As			0.5-2.0		0.1-1
U				0.2-0.8	

Table 2 Noxious Elements in Wastewater From Processing Plants

Noxious	Processing Plants (mg/l)				
Elements	Lead	W-Mo-Bi	Copper	Antimony	Gold
Pb	0.1-1.2	0.01-0.2		<0.01	<0.5
Cd	0.05-0.6	< 0.01		<0.02	<0.025
Zn	0.1-2.0	0.06-6		0.02	0.2
S^{2-}	1-10	7-15	5-10	160	1-20
ArOH	0.01-10				
F	1-50	1-10			
SS	50-100	100-3000		5000	
Cu		<0.1	0.5-1.5	<0.025	<0.025
As		0.01-0.1	0.5-3.0	0.05	0.3-3
Xanthate			0.5-10		

CASE STUDY

In China, Hunan is one of provinces that the management and treatment of mine wastewater have been early carried out in the nonferrous mines. As early as 1972, Bofang underground copper mine used the ion exchange process to treat the wastewater containing the copper-uranium elements, and

Table 3 Metal Elements in Agricultural Land (mg/kg)

Metal Elements	Sampling Location			
	Caoyuan	Heping	Qingshuitang	Yuelu
Cd	0.8-2.43	1.35-1.69	1.64-4.18	0.73-2.20
	0.33*	0.24*	0.24*	0.30*
Pb	61.0-290.0	58.8-67.8	100.6-276.0	103.5-168.0
	20.0*	31.3*	38.0*	16.75*
Cu		38.3-41.8	25.0-35.0	68.3-77.4
		25.0*	5.4*	18.0*
Zn		300-3550	127.5-401.5	450-473.5
		75.0*	17.8*	60.0*

Notes: * --- The values taken in the same soil at a distance of 10 km from the pollutant source are used to compare the measured pollution level.

Table 4 Concentration of Radiomaterials in Water and Bottom Soil in Xiangjiang River

Elements	Radiomaterial Concentration			4*
	1*	2*	3*	
		In Water		
Natural U,g/l	1-1.25x10^{-7}	2.5-5x10^{-7}	2-4	5-10^{-5}
Ra-226,C/l	4.4x10^{-14}	1.6-7.6x10^{-13}	2.4-22	3x10^{-1}
Total Radio-materials,C/l	4.9x10^{-12}	6.62-31.46x10^{-12}		
Natural Th g/kg	4.4x10^{-8}	10-35x10^{-8}	2-8	1x10^{-4}
		In Bottom Soil		
Natural U g/kg	1-6.25x10^{-3}	1-9.25x10^{-3}		1.7-7.0 ppm
Ra-226,C/l	1.40x10^{-9}	2.1-3.1x10^{-9}	1.5-2.5	2x10^{-9}

Notes: 1* --- contrast values; 2* --- measured values taken

from the middle and lower reaches; 3* --- times higher than contrast values; 4* --- limited concentration of groundlevel water set down in China.

this treatment was rapidly developed into a technical scale. In order to eliminate the cyanide pollution, Baoshan copper mine built the installation which the wastewater from the processing plants was treated with bleaching powder. The flotation process without cyanides or less cyanides is employed in some lead-zinc mines such as Huangshaping, Taolin, Hengdong, Qingshuitang and Longhui mines etc., so that the environmental pollution is greatly reduced.

The mining of nonferrous mines makes the natural environment to be polluted and does the ecological equilibrium to be effected. The main form of manifestation is that the acid wastewater which contains a variety of metal ions pollutes the natural waterways. The treatmental technology is varied with the difference of conditions such as quality and amount of water in wastewater from all kinds of mines. In China,the methods of precipitation, air flotation, filtration, ion exchange, extraction, lime neutralization, sulphidization,high-gradient electric magnetization and reverse osmosis etc. are now used to treat the waste water containing metal ions. In order to manage and treat wastewater from the nonferrous mines effectively, it is important to get at the characteristics of mine wastewater. Generally, this type of wastewater is great in amount, more in metal ion kinds, high in acidity,tremendous in changes of wastewater amount and metal ion concentration with the variation of time, and high in content of slime. Therefore,the suitable measures must be taken, technologically, to treat the wastewater,according to its characteristics. Here outline the management and treatment of wastewater in Bofang and Mayang copper mines and in Shizhuyuan polymetallic mine, respectively.

Bofang Copper Mine

The deposit is the small association of copper and uranium or in Bofang mine. The radioactive wastewater is produced in underground mining and ore processing/melting. In the past years, this kind of wastewater was diluted, then directly discharged into Xiangjiang River so that the water in Xiangjiang River was greatly polluted. There contains the metal elements of uranium, arsenic and copper etc. in the wastewater,shown in Table 5. This mine used the ion exchange process to treat the radioactive wastewater. The first plant for the treatment of wastewater was built in 1971, and the daily capacity was up to 3000-3500 tons, while another plant built in 1979 could treat 6000 tons of wastewater per day. In addition, the purification system was installed so that the technology of wastewater treatment was brought into more perfection.

The mine water was used as the mill/melt plant water, while the surplus water was treated separately. In this way, the treatment of wastewater was greatly reduced, and the recovery of copper processing was increased by 1-2% . The treated water up to the hygienic standard was pumped to the sulfuric acid factory for use in cooling, then the cooling water was transported to the copper melt-plant for use in flushing slag. This practice can make the water reuse and save. The comprehensive treatment of wastewater is shown in Fig. 1.

Table 5 Quality and Amount of Radioactive Wastewater in Bofang Copper Mine (mg/l)

Element Content	Underground Mine	Processing Plant
	3600-4000 m^3/d	3300-4000 m^3/d
U	0.3-0.5	5-10
Suspended Substance		7000
As		5.87
Cu	0.155	37.5
Ca	52.58	
Fe^{+++}	0.26	
Fe^{++}	little	
SO_4^{-2}	70	
HCO_3^{-1}	79.94	336
CO_3^{-2}		124
Ra (C/l)	$5.45x10^{-11}$-$2x10^{-10}$	2-$4.1x10^{-10}$
pH	6	10

The surplus mine wastewater was pumped to the treating station installed with the jig table, and the uranium elements were also recovered from it. 0.015 gram of chlorated barium was added into one litre of drainage from the jig table, then this drainage was discharged into the settling pond for removing Ra. After treating, U$\leqslant$0.05 mg/l , Ra$\leqslant 3x10^{-11}$ C/l and pH = 6 in the wastewater. Such this wastewater can be reused as the industrial water.

The uranium elements in the mine/melt-plant wastewater were recovered through the use of ion exchange process. The sulfuric acid, aggregated chlorine aluminium and chlorated barium used as the settle agent were added into the wastewater and pH value was controlled within the limit of 6-7. The metal elements of U and Ra in the wastewater after treating were up to the discharge standard, shown in Table 6.

In recent years, Bofang mine has treated 5.55 million tons of wastewater and the recovery of uranium elements has been up to 27.9 tons, valued at more than 6.50 million Yuan (RMB). The mine wastewater has been used for the ore processing and melting so that the fresh water can be saved by 2500 t/d , and the water/power, the agent of Ra removal and the ion exchange resin can also be saved by 48000 , 15000 and 177000 Yuan per year, respectively. Through many years' effort, the pollution of wastewater from this mine to the environment, notable to Xiangjiang River,has

been almost eliminated.

Table 6 Results of Wastewater Treatment

		Wastewater Types	
		Mines	Mills/Meltplants
U	In Drained Water,mg/l	$\leqslant 0.05$	< 0.05
	Purification Effy, %	$\leqslant 97$-99	97 - 99
Ra	In Drained Water, C/l	$\leqslant 3 \times 10^{-11}$	$\leqslant 3 \times 10^{-11}$
	Purification Effy, %	94 - 96	94 - 98
As	In Drained Water,mg/l	little	< 0.10
	Purification Effy, %		99.5
U Recovery, %		80 - 95	95 - 97
Suspended Substance, mg/l		No	No
pH Value		6.0	6 - 7
Noxious Substance		Up to Hygienic St.	Up to Hygienic St.

Shizhuyuan Polymetallic Mine

The characteristics of tailing water in Shizhuyuan polymetallic mine are as follows:

1. The content of suspended sustance is high, up to more than 10000mg/l. This tailing water is not apt to naturally precipitate.

2. pH value is high, approaching to 10 .

3. The content of sulfide, COD and fluoride is higher than the discharge standards of industrial wastes, and 1.92-7.04, 110-325 and 12-34 mg/l respectively.

According to the characteristics of tailing water in this mine, it has proved practical to use the precipitation process for treating this kind of water. It has been effective that the sulfate ions are removed away from the wastewater through adding the ferriferrous sulfite. The water is clear and transparent after treating. After settling for fifteen minutes, the treatmental results of wastewater can reach to the discharge standards of industrial wastes, shown in Table 7.

Mayang Copper Mine

Mayang is a small mine that the copper barilla is separated through the

use of single stage flotation, with a processing capacity of 500 t/d .

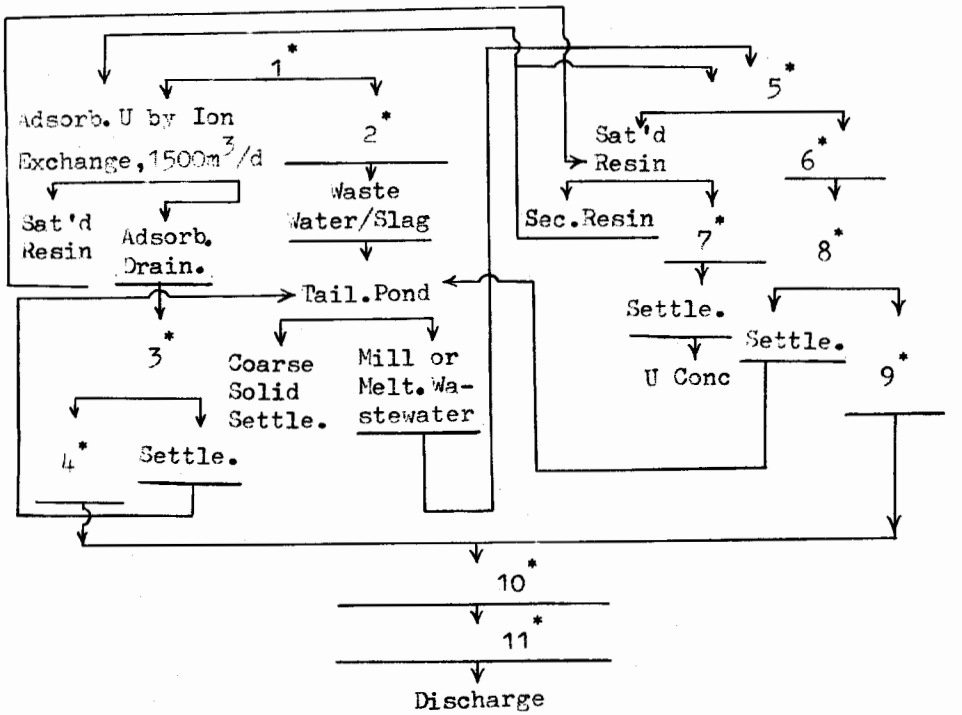

Fig. 1 Flow Sheet of Comprehensive Treatment and Utilization of Radioactive Wastewater in Bofang Copper Mine

Notes: 1* --- mine wastewater, 4000 m^3/d; 2* --- mill or melt plant water, 2500 m^3/d; 3* --- removing Ra by adding Ba; 4* --- water up to hygienic standard; 5* --- adsorbing U by ion exchange; 6* --- adsorbing drainage; 7* --- qualified liquid; 8* --- removing U and Ra by adding the settling agent; 9* --- water up to hygienic standard; 10* --- water used for cooling in sulfuric acid plant; 11* --- water used for flushing slag in copper melt plant.

The wastewater consists of the tailing water (0.4 million m^3/yr), the mine water (100 m^3/d) and other water including the flushing water, cooling water and effluent water from the concentrators etc.(400 m^3/d). The closed-wastewater circuit system has formed and no fresh water is required in the ore processing.

The mine has built a tailing reservoir with a volume of 0.99 million m^3 to precipitate and reuse the tailing water so that the wastewater with

a volume of about 0.15 million m^3 can be converged per year. In addition, the practical management system has been formulated to put the measures of wastewater treatment into effective execution.

Table 7 Results of Tailing Water Treated With Precipitating Process

	pH Value	Sulfide, mg/l	COD, mg/l
Before Treat.	10.1	3.25	139
After Treat.	6.5	0.58	50
First Day	6.7	0.32	50
Second Day	7.1	0.32	49

Through the utilization of wastewater, the power cost can be reduced by 45650 Yuan, and the recovery of ore and copper meltal is 1500 and 7.2 tons respectively, valued at 19000 Yuan, i.e. totalising 64650 Yuan. In addition, the recovery of rougher flotation is up to 83% and the grade of coarse concentrate is 29.06 % Cu, increased by 1.42% and 8.6% respectively higher than that when using the fresh water. The consumption of agent is also reduced, as shown in Table 8.

In Mayang copper mine, the reused rate is up to 70% by means of the utilized measures of mill wastewater. The wastewater reuse is an important way to manage and treat the mine wastewater. However, the technology of wastewater reclamation in China's mines must be futher improved as to catch up with the world advanced level as soon as possible.

Table 8 Comparison of Results of Wastewater With Fresh Water Used in Processing Plants

Separation Ind.,%		Agent Consumption, g/t(ore)			Percentage	
$\sum$Cu	βCu	B.X*1	Sulf. Na	Resinol	W.W.*2	F.W.*3
87.02	19.56	617	195	242	50	50
89.92	25.46	521	95	150	80	20
90.86	23.15	523	40	135	100	0

Notes: *1 --- butyl xanthate; *2 --- wastewater; *3 --- fresh water

MEASURES OF WASTEWATER MANAGEMENT AND TREATMENT

In recent years, the great efforts to manage and treat the mine water

have been made in Hunan. However, the management and treatment of wastewater are not only related to the technology but involved with the managemental measures. The managemental measures of wastewater in the nonferrous mines in Hunan are as follows:

1. Execute Regional Management by Dividing River Into Sections

There are three water systems (Dongting Lake, Poyang Lake and Zhujiang River) in Hunan, in which the water system of Dongting Lake (the rivers of Xiangjiang, Zijiang, Yuanshui and Lishui) distributes over Hunan. The most of nonferrous mines locate at the upper reaches of the three water systems. In order to protect the natural waterways from pollution, the sectors of environmental protection at all levels from the provincial government to the local administrations of mines have taken such measures as dividing river into sections, executing the regional management and assigning the full-time technicians at all levels for this work. In addition, the full- or half-time workers at the regional and communal administrations of countryside are also appointed to do this work.

2. Set up the Perfect Monitoring System of River Basins and Full Control the Pollution of Mine Wastewater

In Hunan's nonferrous mines, the environmental protection has been placed on the agenda, brought into the management of mine enterprises and used as one of acceptance inspection indexes for mine production. According to the rules that ' polluter pays principle ' and ' polluter pays money for the discharge of sewage higher than the standard ',the sector of environmental protection at all levels orders it to treat the pollution within the limited period;if delay,imposes a fine on it. On the basis of the general survey of river basins, all of monitoring stations including ones in mines monitor the pollutants in the basin periodically and have the situation of pollution well in hand timely as to provide more accurate basis for the treatment of pollution.

3. Enhance the Scientific Research on the Management and Treatment of Mine Wastewater

In the light of characteristics of wastewater in the nonferrous mines, the optimal design of treating systems for all mine wastewater has been developed,and the mathematical models and the relation of the environmental benefit for a managemental measure with the socio-economic benefit are sought to establish.

4. Improve the Treatmental Technology of Mine Wastewater

Everything possible must be done to use the new types of technology,agent and equipment so that the treatmental technology of wastewater and the benefits of both economics and environment in the mine development are improved.

CONCLUSIONS

The authors believe the reuse of treated mine wastewater to be significant and to have a good economic benefit in the regions lacking in water resource. In particular, the reuse of treated mine wastewater has a good future. In addition, the mathematical models and the weighted process should be used in the assessment of environmental benefit on the mine wastewater treatment.