ENVIRONMENTAL CONDITIONS IN THE MERCURY MINE OF IDRIA*

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The history of mercury mining in Idria has been excellently described by Teleky (1912) and Kropač (1912). Some historical data on mercury poisoning in Idria is also given by Rosen (1943). From these works the data for the following short historical introduction have been taken.

Mercury deposits in Idria have been known since 1490 or 1497. It is said that mercury in Idria was discovered by a cooper, who found mercury droplets when filling his container from a nearby well. He founded a mining company which was very soon taken over by the local lord. After 1580 the mines became the property of the prince of the province and they were left under the management of the Austro-Hungarian state till 1918, when the Idria district became part of Italy. After the second world war the Idria mines were ceded to Yugoslavia.

Mining was at first in the bituminous shales containing free mercury, but very soon the exploiters turned to cinnabar deposits. The smelting process was very primitive at that time: alternating layers of ore and wood were covered by earth and set alight. The construction of aludel-furnaces, first used in Spain, was an important technological development. In 1785 the Austrian government concluded a trade agreement with Spain and thus undertook to deliver large quantities of metallic mercury. The first measure designed to increase the output of the Idria mines was a regulation providing for the mines and the smelting plant to work all the year through. Before this the smelting plant worked only during three winter months. At the same time the smelting process was improved by the construction of vertical flame furnaces by Leithner in 1787. In 1803 a big fire broke out in the mines and a large part of the pits was flooded. In 1842 the first furnace operating continuously was built in Idria.

Mercury poisoning among Idria miners was described at an early date, one of the first authors

of such descriptions being Paracelsus (1553). Teleky (1912) quotes papers by Pope (1665), Fallopius (1665), Ramazzini (1700), Keyssler (1740), Scopoli (1761 and 1789), Hacquet (1766 to 1773), Hermann (1857) and many others. A very interesting description of mercurialism in Idria comes from Andrea Mattioli in the sixteenth century (Rosen, 1943; Glesinger, 1950). But by far the best and most exhaustive study of this problem is the monograph by Teleky (1912). The problem in the period 1946 to 1950 has been recently described by Hribernik (1950).

Although mercurialism in Idria was very often described from the purely medical point of view, studies of environmental hygiene in the mine and the smelting plant are scarce. Hacquet, a surgeon in Idria from 1766 to 1779, proposed that miners should take hot baths after work and drink milk as preventive measures against mercury poisoning. General body cleanliness, special clothes for work, and the frequent exchange of workers at particularly dangerous working places were measures often recommended by other earlier writers. As far as we know, there was no attempt yet to make a quantitative study of health hazards in the mine and the smelting plant of Idria. The available literature does not offer any data concerning the determination of mercury concentration in the working atmosphere of any other European mercury mine. We do not know whether such air analyses have been performed in the United States, since the report by Davenport and Harrington (1941) was not available.

Technology and Hygienic Problems

In Idria, mercury occurs as cinnabar (HgS) and as native quicksilver. The average content of mercury in the ore is 0.7%. The cinnabar-bearing rock is dolomite, but sometimes also the sandstones of the Wengener group. Native mercury is found in places where dolomite is found in contact with the Geiltal bituminous shales, as well as in the

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CONDITIONS IN MERCURY MINING

FIG. 1.—Winning of native mercury

FIG. 2.—Cinnabar in dolomite

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shales and in the sandstone. It occurs in dolomite very seldom. Mining native mercury is one of the most dangerous occupations in Idria.

Opinions on the genesis of mercury ore deposits differ. It is probable that cinnabar was precipitated from alkaline sulphide solutions. Dreyer (1940) considers that relief of pressure, evaporation of the solvent, and wall rock reactions are the principal factors causing the precipitation of cinnabar. Other authors (Fahey, Fleischer, and Ross, 1940) do not fully agree with Dreyer. There is still much controversy about the origin of native mercury. Kropač (1912) puts forward the hypothesis that the separation of free mercury may have been caused by the presence of iron and its greater affinity for sulphur. Dreyer believes that dilution of cinnabar-bearing solution by surface or juvenile water was the main factor inducing the formation of native mercury deposits; he does not share the opinion that cinnabar might have been reduced to metallic mercury by organic matter. Fahey and others, on the contrary, do not so easily dismiss the possibility that organic matter might have been one of the main causes of the separation of free mercury. This explanation tallies with the findings in Idria where free mercury is encountered in bituminous shales which have a greater reducing power than, for example, coal. (Lack of native mercury in American mines, where cinnabar occurs together with coal, made Dreyer reject the hypothesis of cinnabar reduction by organic matter.) However, it should be pointed out that mineralogical, petrographical and geological conditions of American mines are not identical with those of Idria.

The ore is won by blasting operations, and by hand picking and filling wagons, which are pushed to the main shafts by miners. The further haulage of the ore is mechanized. Drilling and exploratory work in dolomite are performed by pneumatic drills and hammers and wet drilling is not used as present. The winning of free mercury is very dangerous, but there is no hazard where cinnabar alone is dug owing to its slight solubility. Ventilation in the pits is mainly natural; only in a few working places is it mechanical. As dry drilling is accompanied by a terrific amount of dust, the workers in such working places wear dust respirators which, however, do not protect them against mercury vapour or aerosols. Electrical lighting is found only near the main shafts, otherwise carbide lamps are used. Drinking water is available in all sub-levels (galleries) near the main shafts.

According to the mercury content, ore is classified as poor and rich, and, according to size, is separated into coarse and fine ore. This classification takes place in the separation plant before the ore is

subjected to the roasting process. This work is not hazardous, the separation plant being equipped with good ventilation.

Metallic mercury is extracted from the ore by the roasting process. The ore is mixed with suitable fuel and roasted with the access of air. In this way sulphur is eliminated as sulphur dioxide and metallic mercury sublimated. Mercury vapours are diluted by air, sulphur dioxide, and flue gases, and subsequently have to be condensed. There are, of course, mercury poisoning hazards for workers operating the roasting furnaces. Sulphur dioxide is also a potential health hazard, although, compared with mercury, a negligible one.

There are two types of roasting furnaces operating at present in Idria. Shaft-furnaces are used for coarse ore, whilst fine ore and ore dust are processed in specially constructed Čermak-Špirek (or Špirek-Slavik) furnaces. The design and construction of some shaft-furnaces is rather old-fashioned and unsatisfactory from the hygienic point of view. This applies particularly to the construction of the closing mechanism placed on the top of the furnace enabling large amounts of mercury vapour, sulphur dioxide, and dust to escape when the furnace is charged. The double-bell closing mechanism used with some furnaces is more satisfactory, and discharging the furnaces is not dangerous if carried out properly. Incorrect ventilation inside the furnace may represent some danger for workers discharging the furnace. The operation of the Čermak-Špirek furnaces caused few poisonings owing to their special design and to the fact that only fine ore and ore dust are processed. This forms a natural barrier thus preventing the gases from escaping.

On leaving the furnace diluted mercury vapour passes through a system of water-cooled condensing pipes made of earthenware and iron, and enters into the condensation chamber. The condensing pipes are built in the form of inverted U-tubes. Each furnace has its own condensing system which is connected to the main condensing chamber by channels, whence the gases pass to the main chimney. The repair and cleaning of the condensing system, carried out once a month, is the most hazardous work in the smelting plant. Cleaning usually takes six hours.

The condensers yield metallic mercury and so-called "soot" which is a mixture of finely divided mercury and the products of incomplete combustion of fuel (soot, tar, mineral dust, and ashes). "Soot" contains about 80% of metallic mercury and is further processed in Exeli machines with the addition of lime.

Filling steel bottles with mercury for transport is also dangerous owing to the production of fine mercury droplets during this operation.

TABLE 1. RESULTS

1 No.	2 Date	3 Location	4 M.P. Character	5 Operation	6 Ventila- tion	7 Personal Protection	8 t_d (°C.)	9 t_w (°C.)	10 R.H. (%)
1	19.5.50	III.L. 9 G.	●	Hand picking	+	—	25.0	21.0	73
2	17.5.50	III.L. 10 G.	●	Picking (not in work)	+	—	24.0	22.0	84
3	17.5.50	III.L. 10 G.	●	Picking (not in work)	—	—	25.0	23.0	84
4	16.5.50	I.L. 8 G.	◐	Picking (not in work)	—	—	23.5	22.0	88
5	16.5.50	I.L. 9 G. W.P. 1	◐	Picking (not in work)	—	—	21.5	20.0	87
6	26.5.50	I.L. 9 G. W.P. 2	◐	Hand picking	+	—	22.5	21.0	92
7	18.5.50	IV.L. W.P.1	◐	After work	+	—	19.0	17.5	86
8	18.5.50	IV.L. W.P.2	◐	After work	—	—	19.5	17.5	86
9	22.5.50	IV.L. W.P.3	◐	Hand picking	—	—	21.0	18.5	91
10	23.5.50	III.L. 9 G. W.P.1	◐	Drilling	+	Respirator M.S.A.	25.0	23.0	92
11	23.5.50	III.L. 9 G. W.P.2	◐	Hand picking	—	—	23.0	22.0	92
12	20.5.50	VI.L. 4 G. W.P.1	◐	Hand picking	—	—	23.0	21.5	88
13	22.5.50	VI.L. 10 G.	◐	Drilling	—	Respirator M.S.A.	18.5	17.5	91
14	20.5.50	VI.L. 4 G. W.P.2	◐	—	—	—	22.5	21.5	92

native mercury in shale.

cinnabar in dolomite.

native mercury in shale + cinnabar in dolomite.

cinnabar in dolomite + gangue.

OF INVESTIGATIONS IN PIT I

11 w (m/sec)	12 E.T. (°C.)	13 τ (min.)	14 CHg (mg./m ³)	15 C _{max} (mg./m ³)	16 $\frac{CH_g}{C_{max}} \cdot 100$	17 $\frac{CH_g}{Co}$	18 Remarks
0-11	22-5	420	2-00	19-7	10-2	20-0	..
0-16	21-9	120	3-20	18-1	17-7	32-0	..
0-10	22-8	120	5-90	19-7	30-0	59-0	..
0-07	22-3	90	4-50	16-5	27-3	45-0	..
0-08	22-0	90	1-20	14-0	8-6	12-0	..
0-14	20-8	320 240	1-65 1-20	16-0	10-3 7-5	16-5 12-0	Selenium sulphide CHg : 1-15 mg/m.
0-07	17-9	120	1-45	12-2	11-9	14-5	..
0-13	17-0	120	2-30	12-3	18-7	23-0	..
0-16	18-8	120	1-10	14-0	7-9	11-0	..
0-10	23-4	30	0-19	19-7	1-0	1-9	With filter
		30	1-10		5-6	11-0	Without filter
0-18	21-5	180	0-43	16-5	2-6	4-3	..
0-10	21-7	120	0-08	16-5	0-5	0-8	..
0-11	17-4	60	0-05	11-2	0-5	0-5	With filter
		60	0-87		7-8	8-7	Without filter
0-10	21-5	120	0-21	16-0	1-3	2-1	..

The following abbreviations are used in the tables: L = level, G = gallery (sub-level), W.P. = working place, M.P. character = mineralogical and petrographical characteristics of the rock face, t_d = dry bulb temperature, t_w = wet bulb temperature, R.H. = relative humidity, w = velocity of air movement, E.T. = effective temperature (basic scale), τ = sampling period, CHg = mercury concentration in air, C_{max} = saturation concentration of Hg-vapour at the corresponding dry bulb temperature. (Data extracted from tables on mercury vapour pressure, Hodgman, 1946.) Co = maximum allowable concentration of mercury in air, i.e., 0-1 mg./m³ (American Standard, 1943).

TABLE 2. RESULTS

1 No.	2 Date	3 Location	4 Operation	5 Ventilation	6 Personal protection	7 t_d (°C.)	8 t_w (°C.)
1	18.5.50	Shaft furnace I, II, on the top	Charging	Natural	..	20.5	15.0
2	14.10.49	Shaft furnace I, II, on the top	Charging	Natural	..	13.0	10.0
3	19.5.50	Shaft furnace III, IV, on the top	Charging	Natural	..	18.0	14.5
4	22.5.50	Špirek furnace III, on the top	Charging	Natural	..	29.0	20.5
5	14.10.49	Špirek furnace III, on the top	Charging	Natural	..	15.0	11.5
6	23.5.50	Špirek furnace IV, on the top	Charging	Natural	..	27.0	18.0
7	14.10.49	Špirek furnace IV, on the top	Charging	Natural	..	18.0	12.5
8	24.5.50	Under the Špirek furnace	Discharging	Natural	..	24.5	17.5
9	14.10.49	Under the Špirek furnace	Discharging	Natural	..	19.5	14.0
10	23.5.50	Špirek furnace VI	Charging	Natural	..	28.5	19.0
11	17.5.50	Soot-press	Exeli press Working	Natural	..	18.0	12.0
12	15.10.49	Soot-press	Exeli press Working	Natural	..	..	..

OF INVESTIGATIONS IN THE SMELTING PLANT

9 R.H. (%)	10 w (m/sec.)	11 E.T. (°C.)	12 τ (min.)	13 Conc. D	14 Hg Se	15 Remarks
				(mg./m ³)	(mg./m ³)	
54	..	..	480	0.26	0.10	Charging every 3 hours. Continuous sample
69	..	..	30	0.88	..	Sample taken only during charging
69	..	..	480	1.10	0.12	Shaft furnaces are filled with cinnabar ore
46	..	..	360	0.24	0.15	Continuous sample
66	..	..	30	0.33	..	Sample taken only during charging
41	..	..	240	0.88	0.37	Continuous sample
53	..	..	30	0.23	..	Sample taken only during charging
40	0.80	..	480	0.43	0.08	Continuous sample
54	0.10	..	30	0.50	..	Sample taken only during charging
39	0.45	..	240	0.17	0.20	Charging with rich ore (native mercury)
49	0.14	15.5	240	0.82	0.58	..
..	..	..	30	0.68	..	..

TABLE 3
RESULTS OF INVESTIGATIONS IN PIT II

No.	Date	Location	M.P. Character	Operation	Ventila- tion	Personal Protection	t _d (°C.)	t _w (°C.)	R.H. (%)	w (m/sec.)	E.T. (°C.)	τ (min.)	CHg (mg./m ³)	Remarks
1	24.5.50	IX.L. 3 G.		Transport of ore	..	..	17.5	17.0	95	0.17	14.9	120	0.05	..
2	24.5.50	IX.L. 3 G.		Picking (not in work)	..	..	15.5	15.0	95	0.15	13.8	120	0.05	..
3	25.5.50	XII.L. 5 G.		Transport of ore	..	..	..	..	..	..	..	120	0.08	..
4	26.5.50	XII.L. 9 G.		Picking and transport	..	..	20.0	19.0	91	0.25	17.7	120	0.50	30 min. Drilling
5	25.5.50	XII.L.		Drilling	..	Respirator M.S.A.	19.0	17.5	96	0.16	17.0	60	0.10	With filter
												60	0.24	Without filter
6	26.5.50	XIII.L. 12 G.		Transport of ore	..	..	20.0	19.0	91	0.15	18.5	120	0.14	Dust ?

From the point of view of the industrial hygienist the working places in Idria may be divided into three groups: (1) Pit I, where only cinnabar is won, and where no poisoning hazard exists; (2) Pit II, where free mercury occurs beside the cinnabar, and the danger is obvious; and (3) the smelting plant in which especially dangerous operations are the charging of shaft-furnaces, processing of "soot", filling of steel bottles, the monthly cleaning of condensation pipes, and the periodic cleaning of the chimney.

In order to show the scope of health hazards in Idria, we quote some data on mercurialism in Idria from 1946 to 1950 (Hribernik, 1950). In 1946 there were 81 cases of poisoning (seven severe). In 1947 the number of workers poisoned by mercury fell to 27 but in 1948 this figure was again higher and reached 51. In 1949 Hribernik reported 93 cases, and in the first half of 1950 there were 53 poisonings. All these cases were subacute, chronic, or chronic-stationary poisonings.

Evaluation of Hazards

The Institute of Industrial Hygiene of the Yugoslav Academy of Sciences and Arts in Zagreb undertook to investigate the possibilities of making the working environment in the Idria mines less dangerous to the miners' health. The first part of this programme was the determination of the average concentration of mercury in the air breathed by the miners and the smelting plant workers, and the measurement of thermal environment. These investigations were carried out in two parts, in October, 1949, and in May, 1950. The measurements relate to 28 working places, and 43 air samples were taken for the determination of atmospheric mercury.

Analytical Methods

Thermal Environment.—Dry and wet bulb temperatures were measured by means of a sling hygrometer. The air velocity was recorded with a heated-thermometer anemometer (Yaglou) and a kata-thermometer (38–35°C). The relative humidity and the effective temperatures were then calculated. The effective temperature was evaluated by means of a nomogram (Bedford, 1946) calculated against the basic effective temperature scale, as most miners work stripped to the waist.

Determination of Mercury.—Mercury may enter the body by inhalation and by absorption through the skin and the mucous membranes. It is, however, the atmospheric mercury that causes most trouble. Mercury in air may occur as mercury vapour, as mercury aerosol, or as mineral dust contaminated with metallic mercury. All three forms of atmospheric mercury present a health hazard. Therefore, we had to apply an analytical method by which it was possible to estimate the total mercury content in the working atmosphere. We used

the colorimetric dithizone method as described by Milton and Duffield (1947) with slight modifications.

The samples were taken by aspirating air through two midjet impingers connected in series and filled with 5 ml. absorbing solution (4 ml. of bromine in 100 ml. of 8% NaOH) each. Glass beads were put in the impingers in order to increase the absorption surface and to reduce the foaming. The air was aspirated through the impingers at a speed ranging from 0.5 to 1.6 litre per minute by means of hand and electrically driven pumps. The sampling period varied from 30 minutes to eight hours. The size of samples ranged from 30 to 580 litres of air. (The size of each sample was checked separately by means of a precision wet-meter and the manometer attached to the pump.)

The sampling period in the pits was usually two hours. The procedure was as follows:

The air was drawn through the impingers for 30 minutes, then followed an interval of about one hour. This was repeated four times within the working shift of eight hours. In places where much dust was produced (for example, in drilling and exploration work) a fibrous filter ("Whatman" filter paper No. 42) was attached to impingers in order to prevent the dust from entering the absorption liquid. In the smelting plant continuous samples of four to eight hours were taken.

All colorimetric measurements were performed with a Beckman spectro-photometer at the wavelength of 450 mμ.

In some working places, where electricity was available, the concentration of mercury vapour was estimated by means of a "General Electric" selenium sulphide mercury vapour detector. This indicator is sensitive to mercury vapour only, but not to mercury aerosols. The advantage of this method is that selenium sulphide paper does not react with cinnabar dust.

Results.—The results of measurements are given in Tables 1–3.

The data have been calculated assuming that all atmospheric mercury exists as mercury vapour, which is not strictly correct. However, "saturation" as defined in the heading of column 16, Table 1, is a very useful parameter showing the overall contamination of air with mercury. Mercury vapour concentrations, determined by means of selenium sulphide paper, are noted in the column "Remarks". A special note is put also for cases where a fibrous filter was attached to the sampling apparatus.

Table 2 refers to the smelting plant. Here the concentrations of mercury vapour, obtained by selenium sulphide indicator, are entered in a separate column (Se). Those obtained by the dithizone method are marked by D. The air movement in the smelting plant was also measured, but it changed so rapidly that the results could not be given by a single number, and have therefore been omitted.

Discussion

As shown in the tables, the dry bulb temperature in the Pit I ranged from 18.5 to 25°C, in Pit II from 15.5 to 20°C, and in the smelting plant from 18 to 29°C. Considering that these figures refer respec-

tively to underground working places and to work near roasting furnaces, they are rather low. Data on relative humidity are not so satisfactory. Relative humidities of 73–92% found in Pit I, and of 91–96% in Pit II are very high. The air velocity in Pit I (0.07–0.18 m/sec.) and in Pit II (0.15–0.25 m/sec.) is inadequate owing to the lack of mechanical ventilation which is found in a few places only.

The values of effective temperature range from 17–23.4°C (Pit I) and from 13.8–18.5 (Pit II) showing that overall climatic conditions in Pit II are considerably better than in the Pit I. However, the effective temperature does not give an adequate picture of climatic conditions in the pits. Thus in many working places in Pit I we experienced a feeling of discomfort which may be described as “too hot and stuffy”, although the effective temperature was not particularly high. This was probably due to the fact that the air movement was very low and showed no variability.

Mercury concentrations found are rather high and amount to 0.05–5.9 mg/m³ (Pit I), 0.05–0.50 (Pit II), and 0.17–1.1 mg/m³ (smelting plant). An objection may be raised that these concentrations are in general too high owing to the contamination of samples with cinnabar dust. We had in mind this possibility and we tried to eliminate it as much as possible. Whenever it seemed that contamination with cinnabar was likely to occur, we put a note in the table. It is natural that the values of mercury concentrations obtained by means of selenium sulphide indicator are lower than those obtained by the dithizone method, but it does not necessarily mean that dithizone samples were contaminated by cinnabar, as we have to bear in mind that the selenium sulphide does not react with mercury aerosols. In general the results agree well with medical experience concerning the relative danger at different working places. The results obtained in October, 1949, fully correspond to those obtained in May, 1950.

General hygienic conditions in the Idria mines are satisfactory. The washing and toilet facilities are adequate. Hot showers are always available after work. There are also good wardrobes where miners change their working clothes before leaving the plant. Those working at dangerous points receive an extra ration of bacon. There is a part-time medical officer, who examines twice a month

all those working at danger points. On the basis of these periodical examinations, those workers who show any symptoms of mercury poisoning are immediately withdrawn, or given other jobs presenting no mercury hazard. Further medical control consists in the frequent alternation of workers at exposed places. Thus in Pit I, Level I, the miners are changed every four days or sooner if necessary. All work in a mercury-contaminated atmosphere is carefully recorded. Workers performing dusty operations wear dust respirators (usually of Mines Safety Appliances type). At present there are, however, no respirators against mercury vapour in use.

Although the information obtained so far from our investigations is incomplete, it nevertheless suggests some further protective measures, such as (1) the improvement of ventilation (Pit I), which would reduce the concentration of mercury in air to a certain extent, and at the same time make thermal conditions better; (2) the use of respirators against atmospheric mercury (in such operations as winning native mercury, charging furnaces, and cleaning the main chimney); (3) the use of hose-masks for cleaning of condensers; and (4) wet methods in drilling.

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