

ASSESSMENT OF POTENTIAL HEALTH HAZARDS DURING EMISSION OF HYDROGEN SULPHIDE FROM THE MINE EXPLOITING COPPER ORE DEPOSIT – CASE STUDY

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SUMMARY

Aim: The aim of this study was to determine hydrogen sulphide concentration emitted from the mine extracting copper ore, to evaluate potential adverse health effects to the population living in four selected villages surrounding the exhaust shaft.

Materials: Maximum measured concentration of hydrogen sulphide in the emitter is 286 $\mu\text{g}/\text{m}^3$. Maximum emission calculated from the results of determinations of concentrations in the emitter is 0.44 kg/h.

Results: In selected villages hydrogen sulphide at concentrations exceeding 4 $\mu\text{g}/\text{m}^3$ was not detected in any of the 5-hour air samples. In all locations, the estimated maximum 1-hour concentrations of hydrogen sulphide were below 1 $\mu\text{g}/\text{m}^3$, and the estimated mean annual concentrations were below 0.53 $\mu\text{g}/\text{m}^3$.

Conclusion: Any risk to the health of people in the selected area is not expected. As indicated by the available data on the threshold odour, the estimated concentrations of hydrogen sulphide may be sensed by humans.

Key words: hydrogen sulphide determination, copper ore mine, model estimation, odour

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INTRODUCTION

Copper deposit in south-western Poland (Legnica-Glogow District), originate from sediments of the Permian period. The series of ore in the form of dark deposits rich in organic matter and containing metal sulphides, or as deposits with red spots devoid of organic matter are carriers of iron oxide. Room pillar technology is used to extract copper ore in the underground part of the mine. The room pillar technology involves breaking the ore using explosives, taking the winning from the mine face, bringing it by diesel-powered machines to the loading spots, placing it on conveyor belts to convey it to the region of the output shaft, pre-crushing of the copper ore and bringing it through the output shaft to the surface. In the mine headings where the ceiling layers are located close to the anhydrite rock, leakage of subsurface natural gas has been occasionally recorded. Pollutants lifted into the mine ambient air during the mining operations are discharged with the air into the atmosphere. Mine headings are ventilated using the ventilation system consisting of air supply shaft that supplies fresh atmospheric air to the underground headings and exhaust shafts discharging the polluted air from the headings to the outer atmosphere.

Emissions of gases and vapours, which can cause unpleasant sensations of smell is an important issue for people living close to the exhaust shafts. Air pollution is the reason for subjective reactions of the inhabitants which are reflected in the complaints addressed to different offices managing the environment. Ac-

cording to the data obtained from the Ministry of Environment in 2013, as much as 1,323 air pollution complaints were recorded in Poland; of those, 869 (over 65.7%) referred to odour. Unfortunately, inhabitants cannot start effective action, because current regulations do not contain instruments that would make possible to assess if odour intensity is below or above the permissible limits. It is expected that the problem will increase. At the end of January 2014, the Ministry of the Environment granted a license for further exploration and prospecting of copper ore deposits.

In the USA, investigators have recently found connection between coal production and adverse health effects, including increased risk of respiratory diseases among residents of the area affected by emissions (1). Sulphide is liberated as a gas, creating conditions in coalfield homes where short-term and long-term exposures can exceed applicable health standards.

The aim of this study was to determine hydrogen sulphide concentration emitted from the mine extracting copper ore to evaluate hazard and annoyance associated with emission and immission of this chemical as well as to assess the risk of potential adverse health effects to the population living in the area surrounding the exhaust shaft.

MATERIALS AND METHODS

The subject of the study is an underground mine operating copper ore deposit within the mining areas on the border of the

municipalities Radwanice and Jerzmanowa in the area of Sieroszowice. The population of the Jerzmanowa municipality is approximately 4,000 and the area is 63.5 km². The southern border of the square shaft is adjacent to a large forest complex and the remaining sides of the square shaft are surrounded by agricultural land – mostly arable. On the northern and north-eastern side of the shaft area approximately 1 km from the nearest emitters, there are areas of the densely inhabited villages of Jakubow and Maniow. At a distance of about 1.6 km north-west from the nearest emitters runs the southern border of the forest nature reserve Buczyzna Jakubowska.

The tests were carried out in the shaft used to remove the stale air from the mine headings, equipped with a ground station provided with 4 axial fans. The nominal capacity of each fan is 400 m³/s. The fans were connected to individual diffusers with outlets at the height of 36.3 m, the surface area of the outlet cross-section being $S = 46.6 \text{ m}^2$. During normal use, 3 fans are operative, and the fourth serves as a reserve. The purpose of ventilation is to remove air polluted during mining work as a result of diesel fuel combustion, detonation of explosives, handling and transport of the winnings, and maintenance works.

For quantitative determination of hydrogen sulphide in the exhaust diffuser, a method was used in which hydrogen sulphide absorbed in the solution of zinc acetate reacted with N,N-dimethyl-p-phenyldiamine in the presence of iron (III) chloride to form methylene blue serving as the basis for spectrophotometric determination. The method characterized by the lower limit of quantitation (LOQ) of 0.05 µg/ml of the solution of absorbent and allowing collection of up to 600 litres of air was used (2, 3). Air samples for the determination of hydrogen sulphide were collected from the diffuser to the scrubber absorbent solution (acidic solution of zinc acetate) protected from light with aluminium foil. A total of 20 samples were collected at two levels of the diffuser. Samples were collected at a constant volume flow rate (VFR) of 20 l/h, for 30 minutes. Additional 5 samples were collected by insulation methods into 10 liters Tedlar® bags covered with aluminium, head-space vials. The air from the bag then passed through a scrubber absorbent solution and assayed for the concentration of hydrogen sulfide as in the case of earlier samples.

Immission measurement sites were selected within walking distance from the emitter as a result of reconnaissance – the intensity of the characteristic odour of sulphur compounds served as the criterion for selection of the sampling site. Unpleasant sensations of smell for people living close to the exhaust shafts were found in these villages: 2.06 km E (Jerzmanowa), 3.35 km NW (Bukwica), 3.3 km SW (Przesieczna), and about 5 km NE (Jaczow). The tests were carried out in summer. At selected sites, 24 air samples were collected for the determination of hydrogen sulphide. In each of the measuring points five samples of air were collected successively with a volume of 60 l with a constant VFR 60 l/h and simultaneously one 5-hours sample with a volume of 300 liters was collected. Based on LOQ corresponding maximum hydrogen sulphide concentrations in the air were equal to 20 µg/m³ and 4 µg/m³, respectively. The methodology described above was used for collecting the samples of the air in selected locations.

The calculations of the distribution of hydrogen sulphide released from the shaft into the ambient air were performed using the Gaussian Dispersion Modelling – ZANAT® software package compatible with the ordinance by the Minister of Environment of

26 January 2010 on the *Reference values for certain substances in the air* (4). The software enables calculations of atmospheric air pollution resulting from the activities of the arrays of the point, the linear and the surface emission sources.

Maximal concentration S_m (µg/m³) of a gaseous substance averaged over one hour in specified atmospheric conditions is calculated from the formula:

$$S_m = C_1 \frac{E_g}{uAB} \left(\frac{B}{H} \right)^g \times 1000$$

Where:

E_g – maximum emission

C_1 – tabularized constants dependent on atmospheric equilibrium

A – indicator of atmospheric horizontal diffusion

B – indicator of atmospheric vertical diffusion

u – wind speed

H – effective height of the emitter

Maximum emission (E_g) was calculated from the results of determinations of concentrations in the emitter. Indicators of horizontal and vertical diffusion (A, B) are calculated by ZANAT® in each of mesh node, depending on parameters such as effective height of the emitter, average aerodynamic roughness of the area around the emitter and coefficients of state of equilibrium atmosphere. Effective height of the emitter (H) depends on geometric height and diameter of emitter, offgas velocity and temperature. Meteorological data (windrose) necessary for the calculations were obtained from the Institute of Meteorology and Water Economy. In immission modelling, the following parameters based on information received from the contractor were assumed: emitter equivalent diameter 9.97 m, offgas velocity 5.49 m/s, offgas temperature 293°K, average aerodynamic roughness of the area around the emitter 1.09. For the purpose of the calculations the area of 10 x 10 km was applied, which included the villages selected for the analysis. Background level for H₂S was set at 10% of the reference values averaged over one year. In Poland, the reference values for hydrogen sulphide that are unlikely to cause adverse health effects in the general population are 5 µg/m³ (averaged over the period of the year) and 20 µg/m³ (averaged over one hour).

RESULTS

Maximum measured concentration of hydrogen sulphide in the emitter was 286 µg/m³. Maximum emission (0.44 kg/h) was calculated from the results of determinations of concentrations in the emitter taking into account gas volume flow in the emitter equals 20 l/h.

At selected sites of Jerzmanowa, Bukwica, Przesieczna, and Jaczow, on measurement days in any of the 1-hour air samples, hydrogen sulphide was not detected at concentrations exceeding 20 µg/m³ and simultaneously in any of the 5-hour air samples, hydrogen sulphide was not detected at concentrations exceeding 4 µg/m³.

The largest model-estimated maximum concentration of hydrogen sulphide averaged over one hour (taking into account the assumed background level of 0.5 µg/m³) was 1.91 µg/m³, corresponding to less than 10% of the reference value, and it was found in three points, within about 141 m south-east, north-east

In all selected villages, the estimated maximum 1-hour concentration of hydrogen sulphide was below $1 \mu\text{g}/\text{m}^3$, the lowest in Jaczow, below $0.8 \mu\text{g}/\text{m}^3$ (Fig. 1).

Distribution of mean annual concentrations of hydrogen sulphide in the immediate vicinity of the emitter shows that the highest estimated mean annual concentration of hydrogen sulphide was $0.628 \mu\text{g}/\text{m}^3$ (including the background), and was located approximately 300 m to the east from the emitter. Concentrations above $0.55 \mu\text{g}/\text{m}^3$ only occur in an area eastward from the emitter at a distance of less than 900 m (Fig. 2).

Model-estimated mean annual hydrogen sulphide concentrations in all selected villages were below $0.53 \mu\text{g}/\text{m}^3$ including background.

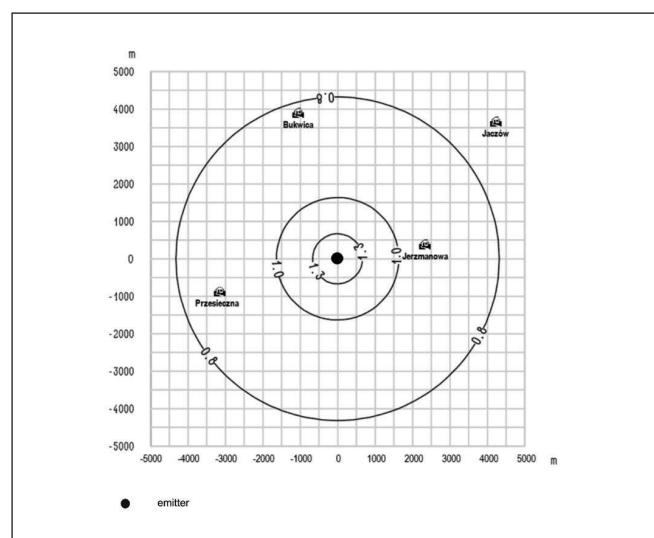


Fig. 1. Model – estimated maximum 1-hour concentration of hydrogen sulphide in selected village.

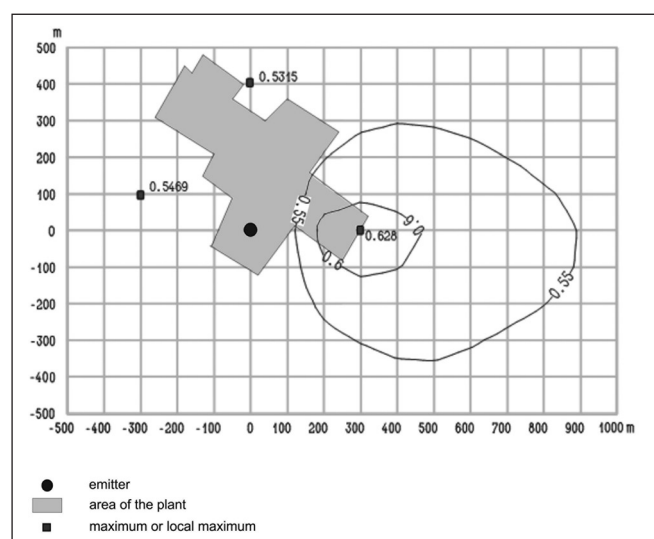


Fig. 2. Model – estimated mean annual concentration of hydrogen sulphide in the immediate vicinity of the emitter.

In normal conditions, hydrogen sulphide is a gas characterized by a repulsive odour of rotten eggs. The central nervous system and the lungs are the major target organs in acute poisoning with hydrogen sulphide. Common complications include bronchopneumonia and pulmonary oedema (5–11).

Low concentrations result in painful inflammation of the conjunctiva and corneal erosion, irritated nose and throat, and bronchitis. A number of neurological and neuropsychological changes following the acute toxicity have been recorded (2). Some epidemiologic studies have reported compromised cognitive and sensory performance among individuals exposed to low concentrations of hydrogen sulphide. In separate exposure sessions administered in random order during three consecutive weeks, 74 healthy subjects were exposed to 70 $\mu\text{g}/\text{m}^3$ (0.05 ppm), 700 $\mu\text{g}/\text{m}^3$ (0.5 ppm) and 7,000 $\mu\text{g}/\text{m}^3$ (5 ppm) H_2S . During each exposure session, subjects completed ratings and tests before H_2S exposure (baseline) and during the final hour of the 2-hour period. Increases in ratings of odour intensity, irritation and unpleasantness were observed. Total severity of the symptoms was not significantly elevated across any exposure condition, but anxiety symptoms were significantly higher in the 7,000 $\mu\text{g}/\text{m}^3$ than in the 70 $\mu\text{g}/\text{m}^3$ condition. Increased anxiety was significantly related to ratings of irritation due to odour. Analyses revealed significantly increased ratings of intensity at 80 and 90 min for pairwise comparison of all exposure conditions and for pairwise comparison at 100 min of 0.05 ppm to 0.5 ppm, and of 0.05 ppm to 5 ppm. This study confirmed that at environmental concentration 70 $\mu\text{g}/\text{m}^3$, subjects rate the odour as more intense than baseline air (13).

It is believed that hydrogen sulphide at a concentration of 6.6 $\mu\text{g}/\text{m}^3$ is sensed by 50% of subjects as the smell of rotten eggs (14). The concentration of 0.7 $\mu\text{g}/\text{m}^3$ is considered “odour threshold low”, 14 $\mu\text{g}/\text{m}^3$ “odour threshold high” (15), while 11 $\mu\text{g}/\text{m}^3$ is the geometric mean value from 26 source data (16).

Relative to control communities, Legator et al. (17) reported higher odds ratios for 9 of 12 symptom categories with the highest odds ratios for central nervous, respiratory and blood systems (e.g. clotting disorder, bruising, anaemia) among residents living in communities in Texas and Hawaii, where maximum 2-hour H_2S concentration of 140–280 $\mu\text{g}/\text{m}^3$ and 280–700 $\mu\text{g}/\text{m}^3$, respectively, were documented. A study of residents from Rotorua, New Zealand, where H_2S exposure associated with geothermal energy was documented in the community, reported increased incidence of nervous system and sense organ diseases (18, 19).

Jaakkola et al. (20) reported that exposure to hydrogen sulphide in people living in the area with the pulp-mill caused 12 times more eye irritation compared to people not exposed to hydrogen sulphide. These effects were observed at the mean annual hydrogen sulphide concentration of 6 $\mu\text{g}/\text{m}^3$. However, the reported ocular symptoms may have been caused by the exposure to peak concentrations of hydrogen sulphide (daily peaks as high as 100 $\mu\text{g}/\text{m}^3$) or co-exposure to methyl mercaptan and methyl sulphides.

Series of studies reported the results of the South Karelia Air Pollution Study which, in the year 1986, began to evaluate the effects of a low-level mixture of air pollutants on human health from the pulp mills in South Karelia and elsewhere in Finland (21). These studies have demonstrated that low levels of hydrogen sulphide in combination with other sulphur-containing pollutants

and, possibly, in combination with particulates and/or sulphur dioxide can have an adverse effect on respiratory health. However, at present they are not able to tell whether this means the low annual average total reduced sulphur (TRS) levels at $1.2 \mu\text{g}/\text{m}^3$ or the daily average concentrations $56 \mu\text{g}/\text{m}^3$, which are associated with these findings. The levels measured in Ružomberok neighbourhood foreshadow quite similar results (22).

According to WHO health risk depends on short-term concentrations of hydrogen sulfide. WHO establishes ambient air quality level for H_2S of $150 \mu\text{g}/\text{m}^3$ during 24 hours averaging period. It is derived from the lowest adverse effect level of hydrogen sulphide of $15 \text{ mg}/\text{m}^3$, when eye irritation is caused, taking into account a relatively high protection factor of 100 (23).

Application of the Provisional Advisory Levels (PALs) protocols was performed for hydrogen sulphide as experimental data permitted. PALs are a tiered set of exposure values used to inform risk-based decision making during a response to environmental contamination involving hazardous chemicals. There are advisory levels for exposure to chemicals of the general public (including susceptible and sensitive sub-populations), developed for the following exposures to contaminated air and water. Three levels distinguished by severity of toxic effects are developed for inhalation exposures for the general public: PAL 1 (mild, transient, reversible effect), PAL 2 (serious, possibly irreversible effect), and PAL 3 (severe effect or lethality). H_2S inhalation PAL values for 24-hour exposure are PAL 1 = 1.2 ppm ($1.7 \mu\text{g}/\text{m}^3$); PAL 2 = 7 ppm ($9.7 \mu\text{g}/\text{m}^3$); and PAL 3 = 27 ppm ($37.6 \mu\text{g}/\text{m}^3$); 30-day and 90-day inhalation exposure values are PAL 1 = 0.85 ppm ($1.2 \mu\text{g}/\text{m}^3$) and PAL 2 = 3 ppm ($4.2 \mu\text{g}/\text{m}^3$). PAL 3 values for 30-day and 90-day exposures are not recommended due to insufficient data. Long-term data were insufficient to estimate 2-year inhalation (24).

At selected immission measuring points (in villages Jerzmanowa, Bukwica, Przesieczna, and Jaczow) in any of the 1-hour air samples, hydrogen sulphide was not detected at concentrations exceeding $20 \mu\text{g}/\text{m}^3$ and in any of the 5-hour air samples hydrogen sulphide was not detected at concentrations exceeding $4 \mu\text{g}/\text{m}^3$. Using ZANAT® the estimated maximum 1-hour concentration of hydrogen sulphide was below $1 \mu\text{g}/\text{m}^3$. It seems reasonable to assume that concentrations of hydrogen sulphide in atmospheric air, those estimated from the determinations of the emission as well as those detected during the measurement days in the air of the selected sites do not result in hazards to the health of the residents. Due to its foul smell, hydrogen sulphide may be regarded as a slight annoyance to the inhabitants of the studied area. The Gaussian Dispersion Modelling has shown that maximum 1-hour concentration $0.7 \mu\text{g}/\text{m}^3$ – probably the lowest hydrogen sulphide odour threshold described in the literature – covers the area of all selected villages.

Attempts to regulate the problem of the population protection against the growing odour nuisance from business operations have been undertaken in many countries. The perception of odours is subjective, and that is why assessment of odour nuisance is difficult. The boundary between the acceptable and unacceptable nuisance is made vague by many factors, such as differences in the sensitivity of individual people to odour, the character of the landscape, economic situation in the region, etc., making it difficult to arrive at satisfactory solutions. The Odour Law has not been yet enacted in Poland or EU countries – standards for

noxious odours have not been set, which is one of the reasons for the rapid increase in the number of complaints addressed, among others, to the Inspectorates for Environmental Protection. Effective legislative action should be undertaken to protect citizens from such noxious factors as odours.

In view of the study purpose mainly the short term (24 hours) data are adequate for health risk assessment. On the other hand in 2000, the U.S. Environmental Protection Agency (EPA) (25) has estimated inhalation reference concentrations (RfC) for hydrogen sulphide at $2 \mu\text{g}/\text{m}^3$ based on the research of Brenneman et al. (26) in rats. Rhinitis was adopted as the critical effect. RfC value is the estimate of the concentration of toxic substance in the air (with a range of uncertainty as high as one order of magnitude), which probably will not result in perceptible risk of harmful effects in the entire human population (including sensitive subgroups), exposed daily by inhalation throughout the whole life span. Uncertainty factor is a parameter used to determine the presumably safe environmental exposure limits for humans. Estimated by ZANAT® mean annual concentration in selected villages is less than $0.55 \mu\text{g}/\text{m}^3$, so it is about four times lower than RfC.

CONCLUSIONS

In summary, the estimated and the determined immission concentrations of hydrogen sulphide in 4 villages located in the vicinity of the copper mine exhaust shaft were many times lower than the relevant existing reference benchmarks defined as acceptable levels of substances in the air plus the margin of tolerance or specified for the protection of human health and for the protection of plants. They do not pose any risk to the health of people living in the area.

As indicated by the available data on the threshold odour of hydrogen sulphide, the estimated concentrations of hydrogen sulphide may be sensed by humans. It would not be reasonable to exclude that in some periods of time an extremely sensitive person may sense odour of hydrogen sulphide in selected village at a short distance from the emitter of the mine extracting copper ore, i.e. 2 to 5 km.

In the next step it would be useful to investigate expected distribution of short term concentrations during the year depending on seasonal influence.

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