

Exposure to chemical agents in aluminium potrooms

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KEY WORDS

Chemical hazards; modernization; aluminium smelter

SUMMARY

Objectives: *To assess the effects of modernization of aluminium production on reducing the chemical health hazards in the working environment in aluminium potrooms (smelter). Modernization included the introduction of a technique of point feeding of alumina and aluminium fluoride into the pots, semi-automatic equipment and computerized control.* **Methods:** *Periodical environmental measurements of chemical substances, dusts containing alumina and fluorides, and gases, i.e., carbon monoxide, carbon dioxide, sulphur dioxide, hydrogen fluoride, nitrogen dioxide, and difluorosulphide, were performed at the same workplaces before (1986-1988) and sixteen years later, after modernization (2004). The measured values were compared with the recommended occupational safety and health standards.* **Results:** *The concentrations of total dust (alumina and fluorides) and gases, i.e., carbon monoxide, carbon dioxide, sulphur dioxide, hydrogen fluoride and phenol, were above the recommended standards in 76.6% (95/124) of the samples before modernization and in only 23.8% (57/240) of the samples tested after modernization. Before modernization in almost all jobs the workers were simultaneously exposed to higher concentrations of all chemical agents present in the working environment. After modernization high concentrations of hydrogen fluoride were the primary pollutant in this plant (GM=4.5451 ppm), while the presence of other gases was significantly reduced. Dusts containing alumina and fluorides and hydrogen fluoride gas were still present in considerable concentrations in the working environments of jobs such as changing and covering of anodes.* **Conclusion:** *The modernization of the aluminium smelter plant reduced the concentrations of the most harmful substances in the working environment and reduced the number of jobs where workers were simultaneously exposed to a variety of health hazards.*

RIASSUNTO

«**Esposizione a sostanze chimiche in una fonderia di alluminio**». *Scopo dello studio è valutare gli effetti delle nuove tecnologie nella produzione di alluminio sulla riduzione dei rischi chimici per la salute negli ambienti di lavoro di una fonderia di alluminio. La modernizzazione consiste della introduzione di una tecnica di alimentazione puntiforme dell'allumina e del fluoruro di alluminio nei forni, di una attrezzatura semiautomatica e della gestione computerizzata. Il rilevamento periodico delle sostanze chimiche, delle polveri contenenti allumina e fluo-*

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ruri e dei gas (monossido di carbonio, anidride carbonica, acido fluoridrico, biossido di azoto, difluorosulfato) nell'aria ambientale è stato effettuato negli stessi posti di lavoro prima della modernizzazione (dal 1986 al 1988) e sedici anni dopo (nel 2004), a modernizzazione compiuta. I valori misurati sono stati paragonati ai valori raccomandati dalle norme per la salute e la sicurezza nei luoghi di lavoro. La concentrazione delle polveri totali (allumina e fluoruri) e gas (monossido di carbonio, anidride carbonica, acido fluoridrico, fenoli) sono risultati superiori agli standard raccomandati nel 76,6% (95/124) dei campioni prima della modernizzazione e solo nel 23,8% (57/240) dei campioni dopo la modernizzazione. Prima della modernizzazione in quasi tutti i posti di lavoro i lavoratori sono stati esposti simultaneamente a concentrazioni più alte di tutte le sostanze chimiche presenti nell'ambiente di lavoro. Dopo la modernizzazione l'elevata concentrazione di acido fluoridrico rappresentava il principale inquinante nell'impianto ($GM=4,5451$ ppm), mentre la presenza degli altri gas è stata ridotta significativamente. Polveri contenenti allumina e fluoruri nonché acido fluoridrico sono tuttora presenti in concentrazioni significative negli ambienti di lavoro quando si sostituiscono gli anodi e si coprono gli stessi. La modernizzazione della fonderia di alluminio ha ridotto la quantità delle sostanze più pericolose negli ambienti di lavoro dove i lavoratori sono contemporaneamente esposti a più rischi per la salute.

INTRODUCTION

The aluminium industry is one of the largest industries in the world today with an annual production of more than 30 million tons. This makes aluminium the world's second most used metal. Aluminium as pure metal or in alloys is used to produce a wide range of products including aircraft, automobiles, domestic appliances and electric conductors. The aluminium industry directly employs over a million workers worldwide.

Primary aluminium is produced by the electrolytic reduction of alumina (Al_2O_3) in large carbon-lined steel vessels called pots, which are housed in "potrooms". The potrooms often extend over several hundred square meters and contain 100 to 300 pots. Pots may be of two types, Søderberg or prebake. The main difference between them is in the way in which anodes are supported. In Søderberg pots, the anode is baked on site and carbon has to be added to the top of the pot. The anodes in prebake pots are produced outside the potroom in a special department. The prebake technology allows for a more automated process, with hoods covering the pot. In modern smelters prebake potrooms are preferred because of the lower levels of emissions (2). In the pots, alumina is partially dissolved in an electrolyte of molten cryolite (Na_3AlF_6) at approximately $980^\circ C$. This is a continuous process that requires large amounts of direct current electrical

power to operate the pots. Periodically, the aluminium is removed from the pots by a process called "tapping" and transferred, still molten, to the cast house.

The production process of aluminium and aluminium alloys in the company *Aluminij Mostar, Bosnia and Herzegovina* begins with the production of liquid aluminium through electrolysis of alumina and takes place in several different plants: *Anode, Electrolysis, Casting and Gas processing plants*. Today, *Alumini Mostar*, rising from the ashes after a five-year war (1991-1995), following reconstruction and modernization, is the most prosperous company in the whole of Bosnia and Herzegovina and is considered the economic giant of south-eastern Europe (8).

Modernization of the *Electrolysis* plant with the introduction of a technique of point feeding alumina and aluminium fluoride into the pots, semi-automatic equipment, replaceable covers on pots, and computerized control, makes it technologically the most advanced production plant of liquid aluminium, and, according to the strict international standards for the safety of workers and the working environment, has greatly improved working conditions. With an annual capacity of 120.000 tons of 99.9% pure aluminium and its alloys, the plant is among the top manufacturers worldwide (12).

In the prebake potrooms, as in the *Electrolysis* plant at *Aluminij Mostar*, there are many jobs, but

the most common ones are tapping and anode changing. Measurement of air contaminants at the workplace is one of most important procedures in the evaluation of exposure to harmful agents in the working environment, as a basis for the health protection of workers.

The main health hazards of jobs in the potroom are chemical, physical, ergonomic, physiological and psychological in nature. The pot fume emissions are complex, and 26 substances to which exposure may occur were listed by Walker (21). Among them, fluorides (dusts and gas from electrolyte bath), dusts (alumina and calcined coke), and gases: carbon monoxide, carbon dioxide, sulphur dioxide, nitrogen dioxide and coal tar pitch volatiles are significant (2, 4). Workers are simultaneously exposed to hazardous physical agents: noise, magnetic fields, and radiation energy (17). Manual tasks involving lifting and incorrect posture may also be performed in many of the jobs in the potroom. These hazards are present in the more common jobs such as anode changing and covering.

The pollutants identified have harmful effects on workers' health. Respiratory disorders were reported as early as 1936 by Frostad, who observed asthma attacks among Norwegian potroom workers (10). Later, the numerous studies made in Europe, Australia and North America among potroom workers described acute airway obstruction ("potroom asthma") and chronic bronchitis (1, 11, 19, 20).

In the present study, we determined and compared concentrations of chemical hazards and their variability over two periods, before and after the modernization. Secondly, we identified the jobs with the highest potential for occupational exposure in the *Electrolysis* plant. The data can be used for improvement of worker safety.

MATERIALS AND METHODS

Mandatory periodical measurements of chemical agents in the working environment in the *Electrolysis* plant were performed before modernization (1986-1988) and in 2004, after modernization of the plant had taken place. Samples were collected,

with fixed samplers, during the 6-hour working shifts over five working days. The average values of measurements of chemicals at workplaces in the plant were taken as the probable value of the true measurement. In both study periods, measurements were made at the same workplaces using the same methods, during the 4 work shifts. The results of measurement were compared with the recommended standards (3, 15).

1. Dust

Dust in the working environment was collected by a fixed aerosol monitoring device (Model 8520, Dust Trak, TSI Incorporated, Shoreview, MN, USA) at different locations in the plant and measured as the concentration of total and respirable dust particles. Dust samples were collected during the 6-hour work shift, over five working days in the presence of the workers. The mean value of the measured concentrations (mg/m^3) was compared with the maximum allowable concentration of the recommended standards (14).

2. Gases

The presence and concentration of gases was measured with a universal device for detecting and measuring the emission and diffusion of gases in the air of the working environment: MIRAN SapphIRE-100/100c (Foxboro Co., Foxboro, MA, USA). The gases measured were carbon monoxide (CO), carbon dioxide (CO₂), sulphur dioxide (SO₂), hydrogen fluoride (HF). During the five days, the measurements were made at different locations in the plant. The mean concentrations (ppm); were compared with the maximum concentrations as per the recommended standards (14).

3. Statistical methods

The chi-square test (or when appropriate, Fisher's exact test) was used for testing the differences in the measured values of chemical agents in the workplace environment before and after reconstruction and modernization of the plant. The level of $p < 0.05$ was considered statistically significant.

Geometric mean (GM) was calculated for the log normal distribution of the measurements. All statistical analyses were performed with Statistical Package for Social Science (SPSS) (11).

Results

The presence and concentration of harmful substances were determined in 124 samples before and in 240 samples after modernization. Concentration of total dust, carbon monoxide, carbon dioxide, sulphur dioxide, hydrogen fluoride, and phenol was measured before (table 1), whereas, respirable dust was measured after modernization (table 2).

Total dust and gases: carbon monoxide, carbon dioxide, sulphur dioxide, hydrogen fluoride, and phenol before modernization showed considerably higher values than the maximum allowable concentration recommended standards (14) in 76.6% (95/124) of the samples, in some, even up to 10 times. Concentrations of total dust (GM=40.211)

and hydrogen fluoride (GM=7,129) exceeded recommended values in 87.5% (21/24), and in 91.7% (22/24) of the samples, respectively (table 1).

The results of measurements after modernization showed that in 23.8% (57/240) of samples the concentrations of gases and aerosols were higher than the maximum allowable concentrations recommended by the occupational safety and health standards. The presence of total dust (GM=11.350) was significantly lower ($\chi^2=19.45$; $P<0.0001$). In two samples the concentration was respectively 6 and 9 times higher than 15 mg/m³, the threshold limit value. Also, the concentrations of gases: carbon monoxide ($\chi^2=25.94$; $P<0.001$), carbon dioxide ($\chi^2=23.35$; $P<0.001$) and sulphur dioxide ($\chi^2=10.077$; $P=0.0015$), were significantly reduced and their presence in the working environment was below recommended values. The higher concentration of hydrogen fluoride (GM=4.545) was detected in 24 out of 28 (85.7%) samples, and the highest concentration was 8 times above the allowed values (table 2).

Table 1. Results of measurement of concentrations of harmful chemical agents before modernization in the Electrolysis plant

Hazards	Concentration of harmful substances				
	N	GM	Range	%> MAC	MAC
Total dust	24	40.2114 mg/m ³	14.1-158.6	87.5	15 mg/m ³
CO ₂	21	5347.6119 ppm	109-14200	71.4	5000 ppm
CO	21	78.1824 ppm	10.0-258.0	76.2	50 ppm
Sulphur dioxide	23	6.6182 ppm	1.7-28.2	65.2	4 ppm
Hydrogen fluoride	24	7.129 ppm	1.9-19.1	91.7	2.5 ppm

N=total number of samples; GM=geometric mean; MAC=maximum allowable concentration; %>MAC=percentage of determinations exceeding the MAC

Table 2. Results of measurement of concentrations of harmful substances in the Electrolysis plant after modernization

Hazards	Concentration of harmful substances				
	N	GM	Range	%> MAC	MAC
Total dust	27	11.3503 mg/m ³	3.1-140.0	25.9	15 mg/m ³
Respirable dust	32	5.6093 mg/m ³	1.18-37.0	40.6	5 mg/m ³
CO ₂	25	0.000 ppm	0.0-2700	0.0	5000 ppm
CO	25	0.000 ppm	0.0-29.8	0.0	50 ppm
Sulphur dioxide	25	0.000 ppm	0.0-9.3	20.0	4 ppm
Hydrogen fluoride	28	4.5451 ppm	0.12-16.9	85.7	2.5 ppm

N=total number of samples; GM=geometric mean; MAC=maximum allowable concentration; %>MAC=percentage of determinations exceeding the MAC

Tables 3 and 4 show the measured concentrations of harmful substances according to jobs. Before modernization, workers were exposed to the highest concentrations of dust and gases at all jobs. During carbon anode changing the concentration of harmful substances exceeded the allowed value in 95.1% (39/41) of samples. For these jobs the measured concentration of total dust (GM=41.382) and gases was higher, more than 10 times for dust and 7 times for hydrogen fluoride (GM=11.308). During anode covering higher concentrations of harmful chemicals were measured in 91.8% (34/37) of samples. For these jobs the measured concentration of total dust

(GM=69.0527), carbon monoxide (GM=107.615) and hydrogen fluoride (GM=7.7975) exceeded the allowed values in all samples. In "tapping" processes when the aluminium is removed from the pots, the concentrations of pollutants was higher in 62.5% (10/16) of the samples. High concentrations of total dust (GM=16.4264) and hydrogen fluoride (GM=3.6676) were also measured in the working environment when pots were closed (table 3).

After modernization, the jobs where workers can simultaneously be exposed to all of harmful substances identified were reduced. However, during anode changing (GM=7.661) and anode covering

Table 3. Airborne concentrations of chemical agents for different job titles in the Electrolysis plant before modernization

Airborne concentration of chemical agents mg/m ³ (ppm)				
Job title/ Chemical agents	No. of samples	GM	Range	% > MAC
Anode changing				
Total dust	8	41.3820 mg/m ³	24.1-158.6	100
CO	7	92.5753 ppm	51-258.0	100
CO ₂	7	6782.9869 ppm	5160-12200	100
Sulphur dioxide	7	11.3199 ppm	2.8-26.8	100
Hydrogen fluoride	8	11.3083 ppm	3.2 -19.2	100
Covering of anode				
Total dust	7	69.0527 mg/m ³	20.1-143.8	100
CO	6	107.6149 ppm	55.0-180.0	100
CO ₂	6	6136.0913 ppm	3200-10900	83.3
Sulphur dioxide	7	7.7438 ppm	1.7-28.2	85.7
Hydrogen fluoride	7	7.7975 ppm	2.9-14.6	100
Metal removal tapping				
Total dust	3	17.1213 mg/m ³	14.4-22.9	66.7
CO	3	68.9363 ppm	46-90	66.7
CO ₂	3	5219.4048 ppm	4100-6800	66.7
Sulphur dioxide	3	4.8493 ppm	4.4-13.1	33.3
Hydrogen fluoride	4	9.4154 ppm	6.3-11.3	75.0
Closing of pots				
Total dust	4	16.4264 mg/m ³	14.1-19.3	50.0
CO	3	47.4761 ppm	41-58	33.3
CO ₂	3	2826.2965 ppm	2010-5200	33.3
Sulphur dioxide	4	3.5177 ppm	2.8-4.9	25.0
Hydrogen fluoride	4	3.6676 ppm	1.9-6.2	75.0
Skimming of dross				
Total dust	2	118.2107 mg/m ³	115.2-121.3	100
CO	2	42.3556 ppm	39-46	0.0
CO ₂	2	4156.92 ppm	3600-4800	0.0
Sulphur dioxide	2	3.2939 ppm	3.1-3.5	0.0
Hydrogen fluoride	2	2.2450 ppm	2.1-2.4	0.0

(GM=8.6486), hydrogen fluoride was emitted into the atmosphere in concentrations higher than recommended values in all the samples. Also, in 75% (3/4) of the samples high concentrations of hydrogen fluoride were measured for metal tapping (GM=4.589) and in all samples for pot closing (GM=3.9528). The presence of other gases: carbon monoxide, carbon dioxide, nitrogen oxide and sulphur dioxide, in concentrations above the maximum allowable values, were significantly reduced for many jobs where the workers can be exposed in the *Electrolysis* plant (table 4).

DISCUSSION

The modernization of the *Electrolysis* plant considerably reduced the concentrations of harmful

chemical agents in the working environment by about four times as also the number of jobs where the workers are simultaneously exposed to different hazardous agents. The concentration levels of individual harmful substances fell by up to ten times. In addition, for many jobs in the potrooms, simultaneous exposure of workers to all of these harmful substances was reduced. The atmospheric concentration of chemical contaminants varies in potrooms and usually depends on the technology (18). Our results showed that the working conditions in the *Electrolysis* plant is comparable to the conditions in most modern aluminum potrooms (17, 22). Due to the nature of the aluminium production process, it is impossible to eliminate all the harmful substances using current safety technology (22).

Table 4. Airborne concentrations of chemical agents for different job titles in the *Electrolysis* plant after modernization

Job title/ Chemical agents	Airborne concentration of chemical agents mg/m ³ (ppm)			
	No. of samples	GM	Range	% > MAC
Anode changing				
Total dust	8	41.3820 mg/m ³	24.1-158.6	100
Total dust	7	14.5979 mg/m ³	9.1-19.3	42.9
Respirable dust	10	5.586 mg/m ³	3.6-10.4	40.0
CO ₂	7	947.823 ppm	120-1450	0.0
Sulphur dioxide	7	2.4677 ppm	0.7-4.5	14.3
Hydrogen fluoride	7	7.661 ppm	3.3-16.9	100
Covering of anode				
Total dust	8	14.1082 mg/m ³	6.5-24.1	50.0
Respirable dust	10	8.1656 mg/m ³	3.6-31.8	70.0
Sulphur dioxide	9	3.2453 ppm	1.0-9.3	44.4
Hydrogen fluoride	9	8.6486 ppm	2.7-19.1	100
Metal tapping				
Total dust	4	4.4872 mg/m ³	3.9-10.6	0.0
Respirable dust	5	3.0524 mg/m ³	2.5-4.8	0.0
Hydrogen fluoride	4	4.589 ppm	2.3-14.3	75.0
Closing of pots				
Total dust	5	4.9991 mg/m ³	3.1-9.1	0.0
Respirable dust	4	3.0098 mg/m ³	2.2-4.5	0.0
CO ₂	4	1230.00 ppm	600-1700	0.0
CO	4	0.000 ppm	0.0-5.3	0.0
Sulphur dioxide	4	2.2863 ppm	2.0-2.4	0.0
Hydrogen fluoride	5	3.9528 ppm	2.7-7.4	100
Skimming of dross				
Total dust	2	36.1912 mg/m ³	35.4 -37.0	100
Respirable dust	2	137.4777 mg/m ³	135-140.0	100

Among the pollutants, compounds of fluor pose the most dangerous occupational exposure. The gas produced, hydrogen fluoride, is definitely the most significant of the compounds. Measurements taken before modernization showed a presence of hydrogen fluoride at all workplaces in the *Electrolysis* plant, in concentrations up to ten times higher than the maximum allowable value. After modernization, hydrogen fluoride was still present in concentrations harmful to workers' health, although the measured concentration was much lower. Considerably lower concentrations of hydrogen fluoride in the *Electrolysis* plant are difficult to achieve with standard safety measurement technology. This is confirmed by Norwegian authors, who measured concentration of hydrogen fluoride up to 5.7 ppm (6).

Apart from hydrogen fluoride, dusts are also present throughout the atmosphere of the *Electrolysis* areas. Before modernization, high levels of these pollutants were measured at almost every workplace. However, concentrations after modernization did not exceed the maximum permitted levels, except in jobs such as anode changing and covering. Semi-automatic equipment for cleaning anode butts decreased levels of dust concentration and physical activity. The employee sits in an air-conditioned cabin to use this device. Dust containing fluorides and alumina are the most dangerous as regards adverse health effects. The fluoride level is mostly associated with handling of the bath and raw materials containing fluoride.

Thanks to modernization of the technological processes and the use of coke with a low percentage of sulphur, the presence of sulphur dioxide, carbon monoxide and carbon dioxide was lowered to a minimum and working conditions were achieved that meet modern standards of aluminium production (9).

In many workplaces in the *Electrolysis* plant the workers are simultaneously exposed to both gases and dust, but the exposure depends on the stage of the smelting process. Operating procedures and work practices can have a direct effect on emission control. The quantities and composition of potline emissions are heavily influenced by operating conditions such as the number, duration and frequency of pot openings, the possibility of increasing the

draught on open pots, temperature, electrolyte levels, anode effects, degree of automation, method of crust breaking and cleaning. Also, the hoods have to be removed from time to time when the anode has to be changed. In this situation, large amounts of pollutants are emitted. The job with a high risk for exposure to hazardous substances involves also covering of anodes with ore, metal and bath tapping. The experience and the motivation of the workers and their way of handling materials and equipment may also be of importance. Research in the Swedish aluminium industry also showed that the electrolytic process of alumina produces significant air pollution which is difficult to eliminate (7, 22).

The *Electrolysis* plant has developed formal procedures and work practices to control emissions. These programmes include limits on the number of pots that can be opened at any one time and periodic inspections of hoods and their conditions.

Work in the plant is organized in four 6-hours shifts, which is one way of reducing exposure to adverse factors in the working environment (5). According to the work safety guidelines, workers have to wear personal protective equipment as well as respiratory protection for harmful gases and aerosols (13). Monitoring workers' exposure to harmful substances at the workplace also shows whether enforcement of protective health measures is successful. Systematic monitoring of safety and health reduces the number of work-related accidents and sick leave (16).

Modernization of the *Electrolysis* plant reduced the amount of harmful substances in the working environment and the number of jobs where workers were simultaneously exposed to various hazards. However, exposure to hydrogen fluoride was only partially reduced.

NO POTENTIAL CONFLICT OF INTEREST RELEVANT TO THIS ARTICLE WAS REPORTED

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