FINAL REPORT TO THE MARIA SKLODOWSKA-CURIE JOINT FUND II ON THE CONSERVATION MONITORING PROGRAM FOR THE WIELICZKA SALT MINE

R. P. Hosker, Jr.
Atmospheric Turbulence and Diffusion Division
Oak Ridge, Tennessee

R. Kozlowski and A. Hejda
Institute of Catalysis and Surface Chemistry
Polish Academy of Sciences
Kraków, Poland

G. R. Cass and L. G. Salmon
California Institute of Technology
Pasadena, California

J. D. Womack and M. E. Hall
Oak Ridge Associated Universities, assigned to NOAA/ATDD
Oak Ridge, Tennessee

J. Bednarczyk
Wieliczka Salt Mine
Wieliczka, Poland

H. A. Crosby
National Park Service
Denver, Colorado

S. I. Sherwood
National Park Service
Washington, DC

October 31, 1994

ABSTRACT

The Wieliczka Salt Mine in Poland contains many historic carvings and sculptures in salt, created over the centuries by the miners and other artisans. The mine is listed as an endangered World Heritage site because these unique artifacts are deteriorating because of dissolution by water. A team of U. S. and Polish scientists and engineers conducted a continuous year-long study of temperature and humidity conditions at multiple locations within the mine to determine the likely sources of moisture at key locations, and to make recommendations for mitigation of the threat.

The data show that conditions favoring the precipitation of moisture from the entering ventilation air stream occur between April and October, and that the volume of water condensed in the mine increases rapidly with increasing external temperatures. Chemical sampling indicates that entering air pollutants are deposited on the surfaces within the mine, but that they do not significantly affect the deliquescence point of the salt. However, surface soiling due to airborne particulates is observed. The Kinga Chapel and the Museum are key areas where the seasonal and diurnal oscillations in relative humidity do not exceed at any time the critical relative humidity of 75% above which strong water absorption and dissolution of the salt occur. But St. Anthony's Chapel is the site of strong condensation, with observed humidities of 75% or more, and therefore suffers badly from surface dissolution.

The recommended solution is installation of a suitably sized dehumidification system at the mine ventilation inlet. An independent engineering consultant visited the mine and used the research study's observations to provide hardware recommendations for a system adequate to protect the critical St. Anthony's area, so as to preserve all of the mine's artifacts for future generations.

1.0 INTRODUCTION

The Wieliczka Salt Mine, located near Kraków, Poland, was designated as a site of "outstanding universal value to mankind" under the World Heritage Convention in 1978, and placed on the list of endangered World Heritage sites, in recognition of the serious threat of deterioration of the historic salt carvings therein. The carvings have been created over many centuries by the miners and other sculptors, and represent an impressive body of art works within the hundreds of kilometres of mine passages.

The deterioration of the salt carvings is due to attack by water, much of which is transported through the air. It is well known that salt develops a liquid film on its surface and begins to dissolve when the relative humidity of the surrounding air reaches approximately 75%. Potential sources of water vapor in the mine include moisture from the forced ventilation system, water sources elsewhere in the mine, or even the breath of the many visitors who tour the mine. Protection of the mine and its artifacts could require different strategies, depending on the moisture source. A survey of the Wieliczka Mine carried out in 1989 (Stelzer, 1989) for ICOMOS and UNESCO noted these points, and recommended research to establish the appropriate measures for conservation.

Under a program funded by the Maria Sklodowska-Curie Joint Fund II, under the auspices of the U. S. - Polish Joint Commission, with additional (later) assistance from the World Heritage Center (within the United Nations Educational, Scientific, and Cultural Organization, UNESCO) a study was carried out to perform measurements and analyses within the monument portion of the

Wieliczka Salt Mine to determine the likely source or sources of moisture in the mine, and to make recommendations for the mitigation of the threat. The collaborating research groups included the National Oceanic and Atmospheric Administration (NOAA), the National Park Service (NPS), the California Institute of Technology (Caltech), the Polish Academy of Sciences' Institute for Catalysis and Surface Chemistry (ICSC), and the Wieliczka Salt Mine (WSM).

The study began with an intensive brief exploratory effort in February, 1992 by teams of U. S. and Polish scientists, during which instruments to monitor conditions (principally air flow, temperature, and humidity) and air pollutant concentrations were installed in key locations within and above the mine. These instruments remained in place for a full year, to assess the diurnal and seasonal variability of the data, and were operated by the Polish team. The U. S. and Polish teams then worked together to evaluate the information and prepare a report and recommendations for the mine authorities, so that remedial measures (principally dehumidification of the entering air stream) could be adopted. A U. S. consultant then volunteered to design a suitable dehumidification system for the mine, and to develop cost estimates for implementing the recommendations.

The U. S. team included Dr. R. P. Hosker, Jr., of NOAA's Atmospheric Turbulence and Diffusion Division (ATDD); Mr. J. D. Womack and Mr. M. E. Hall of Oak Ridge Associated Universities (assigned to ATDD); Dr. H. A. Crosby of the NPS; and Professor Glen R. Cass and Ms. Lynn G. Salmon of Caltech. The Polish team included Dr. Roman Kozlowski and Ms. Anna Hejda of ICSC in Kraków, and Mr. Jozef Bednarczyk of the WSM. Dr. Fred N. Kissell and his colleagues of the U. S. Bureau of Mines Pittsburgh Research Center later consulted with the experimental team on its findings. Mr. Wayne Fry of Fry Equipment Company (Denver CO, U. S. A.) provided designs and cost estimates for the recommended hardware after the conclusion of the monitoring and data analysis.

2.0 APPROACH

The general approach was as follows:

1. Install air monitoring equipment.
2. Collect all related existing information.
3. Check equipment and collect data (except chemical) weekly.
4. Make periodic inspections/observations.
5. Adjust program based on observations and analyses of collected data and information.
6. Analyze Wieliczka salt and its water absorption properties.
7. Analyze monitoring data; develop theory; test theory.
8. Draw conclusions; make recommendations; consult hardware specialists; prepare final report.

Figure 1 is a schematic of the relevant portion of the mine's ventilation system; it indicates the direction of air flow, the principal chambers ventilated, and the location of the team's measurement stations. Note that measurement station 3, originally located in the Haluszka Chamber, became a mobile station; it was used in several other locations to explore conditions at other portions of the ventilation system. Table 1 lists the measurement station locations; the station numbers are used in later Figures to identify results at these locations. Chemical monitoring stations, described below, were located near the mine air inlet (near station 7), in the Kinga Chapel, and St. Anthony's Chapel. A fourth chemical sampling station was temporarily located in the Museum during early March, 1992, only.

The ventilation system in the so-called "monument area", the region of concern for this study, is a suction system. A large blower extracts air (about 1000 m^3/min) from the Paderewski vertical shaft. Air flows into this shaft from the Kinga Chapel and the Haluszka Chamber, and from the sanatorium, located far below ground at Levels V and VI. The various shafts and horizontal passages of the mine generally (but not in every case) serve as both personnel passageways and ventilation ducts. Air enters the mine from an inlet located above the Danilowicz vertical shaft, which also provides elevator access to the various levels. The air from the Danilowicz shaft is then divided among the sanatorium ventilation system, the Antonia vertical shaft, and the Museum area. The measurement stations were located in the ventilation system areas of maximum importance.

TABLE 1. Measurement Station Locations

Station	Location	Level	Dates
1	Museum	III	9 March - present
2	Kinga Chapel	II	9 March - present
3	Haluszka Chamber	III	9 March - 1 May
	Bottom (air outlet) of Antonia Shaft	III	1 May - 6 June
	Connection from Danilowicz to Antonia Shafts	I	7 June - present
4	St. Anthony's Chapel	I	9 March - present
5	Top (air inlet) of Antonia Shaft	I	9 March - present
6	Mine air outlet (top of Paderewski Shaft)	surface	9 March - present
7	Mine air inlet (top of Danilowicz Shaft)	15 m AGL	9 March - present

3.0 EXPERIMENTAL EQUIPMENT

Shortly after funding was approved, ATDD and ICSC scientists selected equipment for monitoring atmospheric conditions in the WSM. It was decided to monitor flow speed, air temperature, and humidity at several locations within the mine, and meteorological conditions (wind speed and direction, air temperature, relative humidity, solar radiation, and precipitation) outdoors, near the ventilation shaft inlet, so that changes in the water content of the ventilation air could be determined as the air passed through the mine. Because of the falling cost of data loggers and other computer-based equipment, funds were adequate to procure equipment for six internal stations, plus the meteorological station on the surface.

A battery-operated programmable data logger was selected. Each data logger provided power to the various sensors on a programmable basis to conserve batteries, and performed unit conversions to transform electrical values (e.g., volts, ohms) to scientific units (e.g., temperature in °C). The six in-mine data loggers read the attached sensors every 60 seconds, and 15-minute averages were recorded in internal memory. The data logger at the ventilation system inlet read the meteorological instruments every 10 seconds, and recorded 15-minute averages and statistics. The data loggers were installed in weathertight lockable enclosures. The in-mine systems were securely bolted to the mine walls in either highly visible locations or in inaccessible locations, to reduce theft and vandalism; no instances of either were found.

The data were recovered each week by ICSC scientists using a "laptop" portable computer. Special software was used to query the data loggers via a serial port, and the data were then written on to a floppy diskette. The data diskette was then carried back to the ICSC, where the data were copied into a spreadsheet running on a 386-class desktop computer. Data analysis and report preparation were performed on this IBM-compatible machine. A dot-matrix printer provided both draft and near-letter-quality output for graphs and reports.

Data and interim analyses were transmitted electronically ("e-mail") via BITNET (and later INTERNET) between ICSC and ATDD, and via INTERNET between Caltech and ATDD. Consultation on problems or interpretations of data were also conducted this way, so that the time differences between Kraków and the U. S. sites were unimportant.

Temperature and relative humidity data were obtained within the mine by sensors selected for their good accuracy and long operating life, even in the presence of air pollutants. A porous Teflon filter protected the sensor element from contamination. For initial calibration checks, a chilled-mirror dewpoint hygrometer was used; this instrument provided a fundamental measurement of atmospheric humidity for comparison to other measurement devices. Precision mercury-in-glass thermometers were used to check the temperature sensor readings.

Propeller anemometers with a very low starting threshold were selected for in-mine measurements of ventilation flow rate. In practice, however, the flow rate in most areas eventually selected for instrumentation in the mine turned out to be considerably below the threshold for these anemometers due to the large cross-sectional areas of the ventilation passages; hence only one was actually installed, at the station in the main ventilation outflow shaft.

The instruments for the meteorological measurements above ground were selected for both accuracy and ruggedness. A low threshold propeller-wind vane combination provided wind speed and direction. A temperature/humidity probe was installed in a naturally-aspirated solar radiation shield. A tipping bucket rain gauge was mounted on the tower. A silicon pyranometer measured total incoming solar radiation.

A miniature pressure transducer was installed in each enclosure to measure barometric pressure; this device received switched battery power from the data logger, and its calibration was adjusted to conform to the portable high-accuracy barometer described below.

In addition to the fixed instruments, a number of portable instruments were carried to the WSM for initial survey work, and for periodic calibration checks. A hot-film anemometer with a digital display was used to determine flow speeds at various locations in the mine shafts and ventilation system; this hand-held device was powered by rechargeable batteries, had an extended probe for reaching locations up to several m from the observer, and had an extremely low wind speed threshold. A hand-held, battery powered, portable temperature and humidity sensor with digital display was used for similar survey work, and for periodic calibration checks of the fixed temperature and humidity sensors; exposure to standard saturated salt solutions was used to verify the continued accuracy of this instrument. An ATDD-owned portable, high-accuracy, barometer/altimeter with a digital readout was used to check the pressure instruments.

Originally there were no plans to perform chemical sampling in the mine. Informal discussions between the U. S. and Polish team members, as well as with colleagues elsewhere, suggested that this might be an oversight. No information on air pollutants entering the mine was available, and it seemed possible that those pollutants (especially particles) might alter the hygroscopicity of the salt within the mine, and thereby influence the deterioration process. The situation was discussed with Professor Glen R. Cass of Caltech, whose team had recently performed air pollution sampling in a cavern holding ancient artifacts in China (Salmon et al., 1992). He offered to send a colleague and suitable ambient air quality monitoring equipment to Poland if funding for equipment shipping and travel expenses could be found.

Because Drs. Crosby and Hosker were both forced by other business to depart from Poland earlier than originally planned, it was possible with careful budgeting to provide the necessary transportation funds from the existing allocation. Hence Ms. Lynn G. Salmon was added to the U. S. team, and she arranged to ship four (plus a spare) filter-based ambient air monitoring systems to Kraków, along with dry deposition plates for sampling particle deposition to surfaces.

The Caltech-designed air monitoring systems measured concentrations and chemical composition of airborne particles in both fine (diameter $d \leq 2.1\ \mu m$) and coarse ($d > 2.1\ \mu m$) particle size ranges, as well as the concentrations of selected reactive gases: SO_2, NO_2, HNO_3, and HCl. Each particle sampling set included three filters. A quartz fiber filter was subjected to later thermal evolution and combustion analysis for carbonaceous species (i.e., organic carbon, elemental carbon, and carbonate carbon). One Teflon filter (0.5 μm pore size) from each set was analyzed by X-ray fluorescence for 34 elements (Ag, Al, As, Ba, Br, Ca, Cd, Cl, Cr, Cu, Fe, Ga, Ge, Hg, In, K, Mn, Mo, Ni, P, Pb, Pd, Rb, S, Sb, Se, Si, Sn, Sr, Ti, V, Y, Zn, and Zr). Crustal element concentrations were converted into the concentrations of their stable oxides where appropriate. Non-carbonate crustal element mass concentrations were then estimated by summing the estimated concentrations of SiO_2, Al_2O_3, Fe_2O_3, and MnO, plus the Ca^+, K^+, Na^+, and Mg^+ oxide compound concentrations in excess of those needed to account for the anionic species present. The other Teflon filter was analyzed by ion chromatography for nitrate, sulfate, and chloride ion concentrations, by colorimetry for ammonium ion concentration, and by atomic absorption spectroscopy for water-soluble sodium and magnesium. Details of the preparation and analysis methods are given in Salmon et al. (1992) and Salmon et al. (1994).

Besides the fine and total particle collection just described, the chemical sampler system used the denuder difference method with nylon filters to measure atmospheric HNO_3 and HCl concentrations, and tandem filterpacks for collection of gas-phase SO_2 and NO_2. SO_2 was collected on K_2CO_3-impregnated paper filters; these were analyzed by ion chromatography. NO_2 was collected using triethanolamine (TEA)-impregnated chromatography filters, also analyzed by ion chromatography.

Horizontally and vertically oriented dry deposition plates were also used. Teflon filters were clamped in specially beveled holders to minimize local air flow disturbances, and analyzed like the ambient air sampler's Teflon filters for $SO_4^=$, NO_3^-, Cl^-, NH_4^+, Mg^+, Ca^+, and K^+. Quartz fiber filters mounted in beveled holders were analyzed for organic carbon, elemental carbon, and carbonate carbon particle deposition rates. NaCl-impregnated paper filters and sliced sections of native Wieliczka rock salt were also deployed as deposition substrates.

To avoid prohibitive data collection and analysis costs, the ambient air monitoring systems and deposition plates were operated only for a single 24-hour period every six days during one month in each of the four seasons (i.e., March, June, September, and December, 1992, and again in March 1993).

4.0 EXPERIMENTAL PROCEDURES

The U. S. team arrived in Warsaw late on 16 February, 1992. They visited the Counselor for Environmental, Scientific, and Technological Affairs of the U. S. Embassy in Warsaw, to discuss the project and obtain funds for in-country expenses. The team arrived in Kraków late on 18 February, and learned that the equipment shipped from the U. S. had not yet arrived; the first of many telephone calls to the U. S. was made, to investigate the matter.

The next day was occupied with meetings at the ICSC to discuss the project and earlier related work. On 20 and 21 February, the team toured the mine extensively, and worked with mine personnel to locate good measurement sites and to videotape a badly deteriorated historic area, St. Anthony's Chapel. Dr. Crosby visited the mine library to view documentation of the condition of selected mine areas in prior years. On 22 February, the team was guided on a tour of Kraków to observe instances of pollutant-induced damage to buildings and monuments, and restoration procedures. That evening, Dr. Crosby departed for Warsaw, and for the U. S. on the following day.

On 24 February, the team carried out an air flow and temperature survey of key mine areas using the hand-held hot-film anemometer. Late on 25 February, the equipment shipped from the U. S. finally was released from Customs; it was unpacked and checked that evening. On 26 February, the team began equipment installation in the mine; by late afternoon, three temporary installations were operational within the Kinga Chapel to assess variability of conditions within this large, important, and heavily ornamented underground church which has minimal ventilation. Virtually no variability was observed, so two of the stations were identified for installation elsewhere.

On 27 February, the outdoor meteorological measurement system was installed on the tall tower structure above the mine elevator, close to the ventilation inlet, and a monitoring system was installed in St. Anthony's Chapel using a temporary mount. Three chemical monitoring systems were assembled and installed: one outdoors (near the mine's air inlet), one in St. Anthony's

Chapel, and one in the Kinga Chapel. Dry deposition sampling plates were set out in both chapels.

On 28 February, one of the temporary installations from the Kinga Chapel was moved to the Haluszka Ballroom (a large tall chamber occasionally used for parties), and a system was also installed in the ventilation duct at mine Level I. A location in the ventilation system outlet was identified for monitoring. A chemical sampler was installed in the mine's large Museum. Filterpacks were installed in all but the Museum chemical samplers, to begin monitoring immediately. On 29 February, the initial filterpacks were collected, and videotapes were made of St. Anthony's Chapel and the Kinga Chapel, to document the permanent installations in each. Dr. Hosker departed for Warsaw during the evening, and for the U. S. the next day.

On 2 March, the team mounted an anemometer and monitoring system in the ventilation system outlet duct. Data from six monitoring stations was successfully downloaded to the portable computer. One monitoring system was moved from its temporary location in the Kinga Chapel to the Museum. All four chemical samplers were reloaded with filterpacks and restarted. On 3 March, part of the team went to the mine to unload the chemical samplers; the others went to ICSC to examine the data retrieved from the data loggers the previous day. Procedures and software for handling the data were discussed with Dr. Kozlowski, who oversaw the effort in Poland. On 4 March, the team visited the Conservator of Stone for Wawel Castle, and toured one of the air quality monitoring stations recently established in Kraków.

On 5 March, the team examined the Crystal Grotto (home to multi-cm size single salt crystals) as a possible site for monitoring. Temperature and humidity surveys were performed with the portable instruments. The four chemical samplers in the mine were reloaded with fresh filterpacks and restarted. The monitoring system from the Museum was temporarily removed and carried to ICSC, where the team spent the evening discussing operational procedures, programming, and data retrieval. On 6 March, the team gave a tour of the instrumented sites to mine and conservation officials and to U. S. and Polish EPA personnel. The monitoring system for the Museum was permanently installed.

On 7 March, the team packed equipment for return to the U. S.; they also visited the Michailovich chamber, which is renowned for its wooden cribbing. On 8 March, the remaining U. S. team members departed for Warsaw during the evening, and for the U. S. the following day.

During the year-long monitoring program, the Polish team routinely collected data, changed batteries, checked instrument calibrations, and performed other maintenance functions as needed. They also inspected the data regularly as a quality control measure, and began the initial reduction and analysis of the data. They also slightly adjusted the monitoring procedures, primarily by shifting the location of one station (number 3) within the mine, allowing the exploration of additional areas.

After data were collected for one full year to establish seasonal variability as well as average diurnal variability, the main analysis was carried out, although interim analysis and discussion of results had begun shortly after the data began to flow. Data and correspondence were exchanged by BITNET ("e-mail"). Progress reports were prepared for the Polish authorities in July, 1992, and for the U. S. authorities in September, 1992. Members of the U. S. team visited the mine in June, 1992 (Salmon) and in November, 1992 (Hosker) to view the ongoing effort, inspect equipment, and compare impressions with the Polish team. The monitoring program was concluded in April, 1993, and the equipment was removed from the mine. Some equipment was moved to the Crystal Grotto area, where the unique very large single crystals of salt are endangered by similar moisture problems.

In September, 1993, Dr. Kozlowski traveled to the U. S. to work with his American counterparts for about one week, to evaluate the findings, make recommendations, and begin preparation of a draft report and recommendations for possible remedial measures. He was joined after a few days by Mr. Jozef Bednarczyk, the ventilation engineer for the WSM, to discuss possible remediation techniques with experts at the U. S. Bureau of Mines' Research Center near Pittsburgh. Representatives of the U. S. and Polish teams then traveled to Washington, DC, to present oral reports before officials of the various collaborating agencies.

Shortly afterward, an American specialist in mine air conditioning and dehumidification, Mr. Wayne Fry, volunteered to visit the WSM, and use the results of the monitoring effort to jointly design with WSM ventilation specialists a suitable system for intervention; this was accomplished during late November and December, 1993.

5.0 RESULTS

5.1 Water Uptake by Salt.

Early in the program, salt from the WSM was collected by the Polish team for analysis of its ability to absorb moisture at a given ambient air temperature. A small amount of crushed salt was placed in a vacuum microbalance; vacuum was maintained until a constant weight was obtained, indicating full drying of the salt. Then water vapor was introduced, and the mass increase of the salt due to absorption and the equilibrium pressure were recorded. A sharp increase in water uptake was observed at about 60% RH, and this became very strong above 70%, with some dependence on ambient temperature, as expected. Dissolution of the salt occurred at about 75%, again as expected. In short, the rock salt from the WSM behaved substantially as normal salt (NaCl).

5.2 Changes in Air Temperature Over Yearly Cycle.

Figure 2 illustrates the changes in the temperature of the air entering and exiting the mine over the entire monitoring year. Note that conditions potentially favoring moisture absorption by the salt (higher temperature of air entering the mine than exiting it) occurred between April and October. The maximum difference between the two temperatures was about 13°C. During the cold season, the entering air was heated during its flow through the mine up to about 11.5°C, whereas during the warm season, the entering air was cooled to about 14°C.

5.3 Water Content and Change Between Stations.

The water vapor content of the air (i.e., the absolute humidity, in grams of water per m^3 of air) was calculated from the air temperature and relative humidity data recorded by each measuring station. This was done by estimating the saturation vapor pressure for the observed air temperature using specialized empirical equations for overlapping ranges: low temperatures (-20 to 0°C), intermediate temperatures (-10 to +10°C) and high temperatures (0 to +28°C). After the saturation vapor pressure was calculated for each temperature observed by every station, the water vapor partial pressure was determined from the estimated saturation vapor pressure and the observed relative humidity. Finally, the absolute humidity was calculated from the ideal gas law using the computed water vapor partial pressure and the observed air temperature. The calculations indicate an abrupt increase in absolute humidity with increasing air temperature. The high content of airborne water in warm, humid air during summer is apparently a principal cause of high moisture uptake by the salt deposit and the detrimental dissolution of the salt surfaces.

Figure 3 shows a sample plot of water vapor content for four stations during the week of 12 - 18 March, 1992. Recall that station 6 was at the mine air outlet, and that station 7 was at the air inlet. Station 5 was near the inlet, at the top of the Antonia Shaft, and the data for Stations 5 and 7 were therefore quite similar. Under the prevailing cold, dry exterior conditions (typical winter conditions), the mine was actually adding water to the entering air, so that the exit water content was roughly twice as large as the entering water content. That is, during the winter, the entering air tends to dry the mine.

Figure 4 shows similar information for the week of 23 - 29 April, 1992. Heavy rains between April 25 and 29 produced sharply higher water content in the air entering the mine, leading to an upward trend in the water content of the exit air. By mid-week, the air entering the mine was wetter than that exiting; that is, the entering air was wetting the mine.

Figure 5 shows sample results for the week of 16 - 22 July, 1992. This typical summertime period shows a slow and weak increase in exit water content, with rather high water concentration in the entering air. During the summer, the entering air tends to add water to the mine.

5.4 Humidity vs. Time in Main Chambers.

The data were used to prepare plots of relative humidity (RH) vs. time in the Kinga Chapel, Haluszka Chamber, Museum, and St. Anthony's Chapel. Diurnal cycles and seasonal trends were of special interest. Any excursions of RH above about 70% are potentially dangerous to the chambers and statues or carvings therein, because of the strong moisture absorption by the salt in this range, possibly leading to dissolution at values near 75%.

It is not possible to display all of the data in this report. Figure 6 shows sample data for the Museum (station 1), Kinga Chapel (station 2) and St. Anthony's Chapel (station 4) for the week of 2 April through 8 April, 1992. Rises in humidity in all three chambers are apparent during the daytime hours, and an overall upward and then downward trend is visible for St. Anthony's. Generally speaking, all the chambers are "safe" for this time period; the Kinga's RH remained below 60% except for part of one day near the end of the period, and the Museum only slightly exceeded 60% on most days. St. Anthony's Chapel was significantly more damp, with the RH above 70% a good portion of the time, although it stayed below the critical value of 75%.

Figure 7 shows a similar plot for the week of 23 - 29 April, 1992. Several days of heavy rain occurred between April 25 and 29, and a clear upward trend in RH is visible for all chambers. Note that the diurnal cycle in St. Anthony's Chapel (st. 4) was sharply suppressed by day 5 of the period, when the RH reached about 75%, and began to be nearly constant with time. We speculate that this corresponded to establishment of an equilibrium between saturated salt solution and atmospheric water vapor; extra moisture, such as that introduced by visitors each day, was immediately absorbed by the solution, so that the RH remained quite constant. Direct observations in St. Anthony's Chapel showed, after the beginning of May, water droplets on the chamber walls, and standing water (brine) in the small basins or depressions in the chapel floor.

Figure 8 shows a similar plot for the week of 9 - 15 July, 1992. Diurnal cycles in the Museum (st. 1) and Kinga (st. 2) are evident. The Kinga exceeded 70% RH on weekdays, but the Museum did not. The RH in St Anthony's (st. 4) remained very constant, near 76%, with slight daytime excursions to about 77%. This behavior was observed for nearly all of the late spring and summer months.

The data also suggest that visitors contribute slightly to humidity increases in the chambers during the day, with peaks occurring about 1:00 p.m. Smaller daytime increases were observed on weekends, when there were no large school tours visiting the mine. No daytime maxima were observed on 19 April (Easter Sunday) when the mine was closed to visitors.

5.5 Chemical Analyses.

SO_2 was the principal gaseous air pollutant observed above ground. The 24-hr-averaged outdoor concentrations ranged from below 20 ppb during the summer to 40 ppb during the winter, probably reflecting the increased use of coal during the heating season. The annual average concentration was about 15 ppb. Inside the mine, however, the SO_2 concentrations were negligible; in St. Anthony's Chapel, close to the air inlet, SO_2 concentrations were only about 3% of those outdoors, indicating rapid loss of SO_2 from the air to interior surfaces. Because sulfate salts generally show relative humidities of deliquescence higher than that for NaCl rock salt, this sulfate accumulation on the mine surfaces is not expected to exacerbate the water vapor absorption problem.

NO_2 concentrations ranged between about 1.5 ppb and 5 ppb outdoors, averaging about 2.5 ppb, and were less than 1 ppb indoors. Average HNO_3 and HCl concentrations within the mine were very low, not exceeding 0.1 ppb; low HNO_3 values would be expected because salt is a nearly ideal sink for HNO_3. Nitrate concentrations on the mine surfaces were quite low. This is fortunate because the presence of significant amounts of low deliquescence point nitrate compounds could aggravate the water vapor absorption problem.

The annual average coarse particle mass concentration observed outdoors was 30.4 $\mu g/m^3$; the corresponding fine particle value was 53.3 $\mu g/m^3$. In St. Anthony's Chapel, the mass concentrations were lower than outdoors, at 20.4 $\mu g/m^3$ for the coarse particles, and 29.1 $\mu g/m^3$ for the fine particles. Since the mine's ventilation system has no filtration, the decrease in particle mass concentrations must be due to dry deposition within the mine. In the Kinga Chapel, the annual average coarse particle concentration of 123.0 $\mu g/m^3$ was much higher than outdoors, and probably was due to sources within the mine. The corresponding fine particle concentration in the Kinga Chapel was 48.5 $\mu g/m^3$.

The chemical composition of the particles varied with location and time. Details are available in Salmon et al. (1994). Organic carbon compounds were the most abundant in the fine particles, with significant amounts of ammonium, sulfate, and elemental carbon. The coarse particles included organic carbon and mineral dust, as well as unknown materials.

There is no compelling evidence that air pollution deposition has worsened the water vapor absorption problem in the WSM. However, there is evidence that surfaces, including sculptures, are becoming soiled by deposition of airborne particles. This is visually apparent mainly on those sculptures carved from translucent rock salt and on fixtures made from salt crystals.

6.0 CONCLUSIONS AND RECOMMENDATIONS

1. The climate within the historic part of the Wieliczka Salt Mine was monitored over a full year's cycle. It is believed that the data are adequate to satisfactorily understand the availability of moisture and its uptake by the salt, with subsequent degradation of the historic carvings.

2. Two main areas where water is removed from the air were identified. One is St. Anthony's Chapel and the adjoining chambers. The second is located on mine Level III, close to the outflow of air from the Antonia ventilation shaft.

3. External conditions favoring the precipitation of moisture (air temperatures higher outside than in the mine) prevail between April and October. The volume of water scavenged from the air in the mine increases rapidly with increasing external temperature. The highest volume of water removed (roughly 17,000 liters) was calculated from data for the week of 18 - 26 June, 1992.

4. The microclimates of St. Kinga's Chapel and the Museum are presently satisfactory from the preservation point of view. Neither the diurnal nor the seasonal oscillations exceed the critical relative humidity of 75%, above which strong water absorption and subsequent dissolution of the salt occur.

5. The chemical sampling results indicate that air pollutants are depositing on the surfaces within the mine, but that the deposition does not affect the deliquescence point of the native rock salt. However, soiling of the surfaces due to particulate deposition is observed.

6. The data suggest that the best solution to the cultural artifact damage problem is probably to cool and dehumidify the air entering the mine during the critical summer period by means of an appropriately sized air-conditioning system.

7. An independent consultant has visited the mine and, after reviewing the data and the geometry of the mine's ventilation system, has made specific recommendations for the necessary hardware to dehumidify the entering air stream during the summer months. Details are provided in Fry (1994). The cost is expected to be less than $225,000.

ACKNOWLEDGEMENTS

The authors are grateful for the support of their parent organizations; for the travel and equipment support provided by the Maria Sklodowska-Curie Joint Fund II, under the auspices of the U. S. - Polish Joint Commission, for the measurement program; and for travel and publication support provided by the World Heritage Center (UNESCO) during the analysis phase. The authors also thank Mr. Bruce B. Hicks of NOAA's Air Resources Laboratory for his guidance, helpful discussions, and general enthusiasm for this project; Mr. Richard Cook and Mr. Rene Eppi of the International Affairs offices of the NPS and NOAA, respectively, for their cheerful assistance with Joint Fund matters and guidance on the problems associated with an international collaborative project; and the Science Office of the U. S. Embassy in Warsaw, the staff of the U. S. Consulate in Kraków, and the staff of the Polish Customs Service in Kraków, for their assistance in moving people and equipment into and from Poland. The authors greatly appreciate the interest and helpful consultations provided by Dr. Fred N. Kissell and his colleagues of the U. S. Bureau of Mines Pittsburgh Research Center. Mr. Wayne Fry of the Fry Equipment Company, Denver CO, generously donated his time to visit the mine, discuss the measurements with the research team and mine officials, and design a comprehensive dehumidification system. Finally, we thank the administration and staff of the Wieliczka Salt Mine, for their superb assistance in the conduction of this study, and their tolerance of our interference with their normal operations. We hope that our findings will assist them in the preservation of the Mine's antiquities for future generations.

8.0 REFERENCES

Fry, W., 1994: Mine Ventilation Air Dehumidification Project. A proposal available from Fry Equipment Company, Inc., Denver CO 80219, USA (5 January 1994).

Salmon, L. G., G. R. Cass, R. Kozlowski, and A. Hejda, 1994: Air pollutant intrusion into the Wieliczka Salt Mine (in preparation).

Salmon, L. G., C. Christoforou, and G. R. Cass, 1992: Characteristics of airborne pollutants in the Buddhist cave temples at the Yungang Grottoes, China (in preparation).

Stelzer, H., 1989: Salt mines of Wieliczka. Report on ICOMOS/UNESCO mission, 15-22 July, 1989. 22 pp. plus figures.

FIGURE CAPTIONS

Figure 1. Schematic of Wieliczka Salt Mine ventilation system in the "monumental area", showing flow paths, major chambers and shafts, and monitoring stations for air temperature and humidity.

Figure 2. Changes in temperature of air entering and exiting the mine over the entire year. When the entrance air temperature exceeds the exit air temperature, water can be removed in the mine.

Figure 3. Ambient air water content (g/m^3) as function of time (0 = midnight), for week of 12 - 18 March, 1992, for four Wieliczka monitoring stations. Station 3 is the Haluszka Chamber, Station 5 is the top of the Antonia Shaft, Station 6 is the vent system outlet at the top of the Paderewski Shaft, and Station 7 is the vent air inlet, at the top of the Danilowicz Shaft.

Figure 4. As in Figure 3, but for the week of 23 - 29 April, 1992.

Figure 5. As in Figure 3, but for the week of 16 - 22 July, 1992. Station 3 moved to connecting passage between Danilowicz and Antonia Shafts.

Figure 6. Relative humidity (in %) as function of time (0 = midnight), for week of 2 - 8 April, 1992, for three Wieliczka monitoring stations. Station 1 is the Museum, Station 2 is the Kinga Chapel, and Station 4 is St. Anthony's Chapel.

Figure 7. As in Figure 6, but for the week of 23 - 29 April, 1992.

Figure 8. As in Figure 6, but for the week of 9 - 15 July, 1992.