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OXIDES OF NITROGEN EXPOSURES ACCOMPANYING PICKLING OPERATIONS
313 BUILDING - 300 AREA

The following is a report of an industrial hygiene study of exposures to oxides of nitrogen accompanying pickling of uranium chips. This investigation was conducted in the 313 Building, 300 Area on February 7 and 17, 1949.

PROCESS

The present pickling process, which is understood to be a temporary arrangement, consists of three steps; degreasing in trichloroethylene, pickling in hot nitric acid and finally washing in water. The layout of this operation is shown diagrammatically in Figure I on page 4.

The chips, as received from Chip Recovery, are in bulk form and are transferred to a wire mesh basket which is placed on a monorail conveyor. The basket is then introduced into the degreaser after which it is withdrawn and placed in the pickling tank containing 60% nitric acid at 50°C. When the reaction becomes sufficiently active the basket is removed and transferred to the first rinse tank. Each basket of chips is alternately pickled and rinsed in this manner three times, the final rinse being in the second rinse tank.

Local exhaust ventilation is provided for the pickling and rinsing operations by a modification of the present slot exhaust ventilation system. Canopy type hoods, which project over the rear section of these tanks, have been installed to catch the oxides of nitrogen fume as it is liberated from the baskets of chips.

OXIDES OF NITROGEN

MASTER

Oxides of nitrogen as encountered in the pickling operation exist mainly as NO_2 and N_2O_4 , which, when in equilibrium present a yellowish-brown appearance. Such fumes when inhaled are insidious in character and serious exposures may, therefore, result with little or no warning from body reflexes.

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Short exposures to low concentrations may cause only a temporary irritation of the respiratory tract accompanied by a cough. Continued exposures to low concentrations, however, may reduce the sensitivity to the fume and relatively high concentrations may then be inhaled unknowingly. Systemic effects from excessive exposures follow a latent period of several hours. Within the body inhaled nitrous fumes yield nitrous and nitric acid which produce pulmonary irritation. This may result in upper respiratory tract and/or pulmonary edema, laryngitis, bronchitis or pneumonitis. If pulmonary edema is experienced, this may be followed by pneumonia, bronchiectasis or emphysema as sequelae. Methemoglobinemia may also occur. It has been indicated¹ that slight symptoms may be noticed around 30-40ppm and that exposures from 240-70ppm may be fatal to animals in a short time.

Medical and engineering studies of oxides of nitrogen exposures have shown that atmospheric concentrations should not exceed 25ppm, by volume, for exposures up to eight hours.

SAMPLING

In order to determine the degree of exposure of the operator to oxides of nitrogen fume a series of air samples were collected during normal operation of the pickling process. In most instances the samples were obtained in the breathing zone of the worker. A few were also taken in the immediate vicinity of the tank to determine the extent of contamination which escapes into the surrounding workspace. The results of sampling are shown in Table I on page 3.

VENTILATION

The pickling and rinse tanks are equipped with slot exhaust ventilation which has been redesigned to provide two small canopy type hoods which project over the tanks from the exhaust plenum behind the tanks. This provision increases greatly the effective range of the present exhaust system and results in the removal of the major portion of the fumes liberated.

Observations indicated that noticeable drafts were present in the immediate vicinity of the tanks due to such factors as the proximity of supply ventilation, people walking by and open doors. Such drafts tended to offset the beneficial effect of the tank exhaust ventilation as well as to disturb the trichlorethylene vapor level in the degreaser and cause solvent vapors to spill out into the workspace.

To determine extent of this condition, the flow of air around the tanks was checked by smoke tests and velocity measurements and the results are presented diagrammatically in Figure I on page 4.

1. "The Analytical Chemistry of Industrial Poisons, Hazards and Solvents" by Morris B. Jacobs, Ph.D.

OXIDES OF NITROGEN CONCENTRATIONS

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SAMPLE NO.	DATE	REMARKS	CONCENTRATIONS, ppm
1	2/7/49	Taken in breathing zone of operator during pickling.	14
2	2/7/49	Same as sample #1.	15
3	2/7/49	Same as sample #1.	7
4	2/7/49	Same as sample #1.	7
5	2/7/49	Same as sample #1.	9
6	2/7/49	Same as sample #1 except that the basket was left in pickling solution slightly longer creating heavier fumes.	392
7	2/7/49	Same as sample #1.	14
1A	2/17/49	Fresh acid solution. Sample taken in breathing zone of operator.	7
2A	2/17/49	Same as sample #1A.	11
3A	2/17/49	Same as sample #1A.	7
4A	2/17/49	Same as sample #1A.	38
5A	2/17/49	Same as sample #1A.	4
6A	2/17/49	Same as sample #1A.	29
7A	2/17/49	Sample collected 4' from operator, next to wash tank.	5
8A	2/17/49	Same as sample #7A.	4
8	2/7/49	Same as sample #7A.	7
9A	2/17/49	Sample collected 6' from operator, next to wash tank.	> 600

TABLE I

FIG. I

Note Figures denote air velocity, feet per minute

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DISCUSSION

It can be seen from the findings presented in Table I that excessive concentrations of oxides of nitrogen fumes can occur in the workroom atmosphere during pickling. Of thirteen samples collected in the worker's breathing zone, three exceeded the M.A.C. (Maximum Allowable Concentration) of 25ppm, with the highest exposure being approximately 390ppm. It was observed that in most cases the fumes which escaped into the room were carried away by drafts into the surrounding workspaces. Sampling of this condition indicated that high concentrations of fume may be encountered several feet from the pickling tank. One sample collected six feet from the operator showed that the concentration was in excess of 600ppm. In view of the insidious nature of oxides of nitrogen fume such concentrations should be considered as a serious health hazard from the standpoint of acute exposures.

The presence of nitrous fume in the workroom atmosphere can be attributed mainly to the large volume of fumes liberated and the inadequacy of the present control ventilation. Chips while in the pickling tank produce considerable fume but the greatest quantity is given off when the basket is withdrawn and suspended just above the acid surface to drain. As the basket is lined with a fine mesh screen the acid drains off slowly, thus, permitting large amounts of fume to be given off. It is at this period when most of the fume escapes from the hood. This condition may be minimized by providing a larger mesh screen liner or by increasing the air flow and size of the hoods in the exhaust ventilation system. It is felt that the latter method is most desirable due to the additional benefit which would also be realized by better control of fumes at all times. This can be accomplished by increasing the size of the hoods in all dimensions, particularly the depth, and height and also by increasing the airflow.

Consideration should also be given to extending the height of the stack discharge for the exhaust system. It is understood that under certain atmospheric conditions the fume which is discharged above the roof is often blown back around the building where it creates a problem from recirculation of the workroom atmosphere.

In view of the reported temporary nature of the pickling installation investigated no major changes in techniques or control measures have been made as it is felt that the present exhaust system can be sufficiently improved to produce an adequate reduction in exposures. It is recommended, however, that the present techniques and controls for degreasing and pickling be modified for the new installation to insure healthful working conditions.

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Frank E. Adley
 Frank E. Adley

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