Identification No. 14203-0-0-02-004

INTRODUCTION

This report is based on an investigation made pursuant to clause (1) of Section 4 of the Federal Metal and Nonmetallic Mine Safety Act (80 Stat. 772).

About 10:30 p.m., November 11, 1971, hydrogen sulfide gas was released from a reagent holding tank in the molybdenum flotation section of the Inspiration Consolidated Copper Company's concentrator at Inspiration, Gila County, Arizona. One man died in the concentrator, and two men died in a hospital November 12, 1971. Six other men were hospitalized or received treatment after being exposed to the hydrogen sulfide gas. A security patrolman assisting in the recovery was injured. The names of the victims are shown in appendix A.

The Arizona State Mine Inspector notified the Bureau of Mines of the accident at 7:30 a.m., November 12, 1971; the investigation was started that day.

Information in this report was obtained from visits to the accident scene and interviews with survivors, witnesses, and other company personnel.

A State Plan Agreement was in effect in Arizona during this investigation.

GENERAL INFORMATION

The Inspiration concentrator, owned and operated by Inspiration Consolidated Copper Company, is at Inspiration, Gila County, Arizona.

The concentrator was operated three 8-hour shifts a day, 7 days a week, by 129 men. Operating officials were: R. C. Cole, vice president and general manager; Henry Allen, general superintendent; and Paul M. Musgrove, concentrator superintendent.

Company-owned open-pit mines furnished approximately 20,000 tons of copper ore a day for processing at the concentrator. An average of 1 ton of molybdenum concentrate a day was recovered in addition to the copper concentrates.

In the molybdenum flotation section, the reagent LR-744 or "Nokes Reagent" was used as a copper mineral depressant. The reagent was manufactured by reacting phosphorus pentasulfide with a caustic solution. The major reaction was: $6NaOH + P_2S_5 \longrightarrow 2Na_3PO_2S_2 + H_2S + 2H_2O + \text{heat}$. Normally, an excess of caustic was present to react with toxic hydrogen sulfide formed. The equation $NaOH + H_2S \longrightarrow NaHS + H_2O$ expressed the secondary reaction. With an adequate excess of sodium hydroxide, the generation of hydrogen sulfide was kept to a minimum provided proper mixing procedures were followed.

A 1,200-gallon-capacity mixing tank for the preparation of the reagent was located several hundred feet outside the concentrator building. The tank was equipped with chilled water cooling coils and an electrically powered agitator. A probe-type thermometer to indicate the temperature of the solution was permanently mounted on the outside of the tank.

Instructions for mixing the reagent were posted near the mixing tank. According to those instructions 4 feet of water was put into the tank, and five barrels of sodium hydroxide were added to make the caustic solution. After the temperature of the solution dropped below 40° C., two and three-fourths barrels of phosphorus pentasulfide were added with a cooling period after the addition of each barrel.

A titration was performed after the addition of the five barrels of sodium hydroxide and after the addition of each barrel of phosphorus pentasulfide. A worksheet was provided to record the temperature at various stages and to record the results of the titrations.

Until a few months previous, written company instructions had specified six barrels of sodium hydroxide; however, it was decided that five barrels would be sufficient to suppress the reaction of phosphorus pentasulfide in water. Accordingly, the specified quantity of sodium hydroxide added to the water was decreased from six to five barrels.

From the mixing tank, the reagent was pumped to one of three storage tanks, each of 1,200-gallon capacity, located on a floor approximately 10 feet above the molybdenum flotation floor inside the concentrator building. Each tank was equipped with a wraparound thermostatically controlled electric heater to prevent freezing of the reagent.

Members of the investigation party were:

Inspiration Consolidated Copper Company

Paul Musgrove, mill superintendent
Donald Skufca, assistant mill superintendent
Ralph Bamario, safety director
Joe Perkins, safety engineer

United Steelworkers of America, Local No. 586

Robert Barcon, president
Art Roche, steward

Bureau of Mines

G. H. Weems, supervisory chemist, Denver Field Health Group
E. Levi Brake, mining engineer

DESCRIPTION OF ACCIDENT

At 9:45 a.m., November 11, 1971, the regular day shift reagent mixer started mixing a fresh batch of reagent LR-744. To the specified 4 feet of water in the mixing tank he added five barrels of sodium hydroxide to prepare the caustic solution. According to the information he recorded on the worksheet, the titration result and temperature were both acceptable.

Two barrels of phosphorus pentasulfide, one at a time, were added and again according to the worksheet, the temperatures and titration results were within acceptable limits. The day shift reagent mixer went off shift leaving three-quarters of a barrel of phosphorus pentasulfide to be added to the solution to complete the mixing.

According to Raymond Smyers, afternoon shift foreman, Assistant Shift Foreman Donald Brough, victim, came to him during the first part of the shift and asked if he should take a qualified reagent mixing man away from his assigned duties at another job in order to complete the mixing of the reagent. Smyers indicated they needed to train another reagent mixer for the vacant job and for Brough to take someone else.

About 8 p.m., Brough took Glasco and Roberts, both laborers, to the mixing tank to complete the preparation of the reagent.

Persons familiar with the company mixing procedure stated the two and three-quarters barrels of phosphorus pentasulfide required for each batch were obtained by dumping two full barrels and three-quarters of another full barrel into the tank each time. After three batches had been prepared, there would be three barrels in the storeroom each containing approximately one-quarter of a barrel. The next batch would be prepared using two full barrels and three partial barrels.

According to Glasco and Roberts, three partial barrels were in the storeroom, and on the instruction of Brough, they dumped the contents of each barrel into the solution. Glasco later stated that the first two barrels were considerably lighter and obviously contained less phosphorus pentasulfide than the third barrel.

According to Roberts, who had done this work twice previously, Brough instructed him to dip a sample of the solution from the tank for titration. He did not watch Brough perform the titration but did notice that the final color of the titrated solution was milky white. The normal color should have been amber or yellow. The final titration result listed on the worksheet, apparently in Brough's handwriting, as well as the final temperature, was within the allowable limits.

After the three partial barrels of phosphorus pentasulfide had been added, Glasco stated Brough called him to the tank agitator and pump control switch panel and gave him instructions on starting the tank agitator. Glasco was not sure that the agitator was operating previously.

Shortly after dumping the last of the phosphorus pentasulfide into the reagent solution, Brough started the pump to transfer the reagent to storage tank No. 1. Glasco stated Brough sent Roberts and him to tank No. 1 to see if the solution was entering the tank. They could hear a splashing sound inside tank No. 1 and assumed the solution was entering normally; they reported this information to Brough, and he sent them back to their normal duties. About 9:35 p.m., Brough took Roberts and Glasco back to the mixing tank and stopped the pump, and then they returned to the main concentrator area to continue with belt cleanup work.

One of the characteristics of hydrogen sulfide is that its odor is detectable only in very low concentrations. High concentrations have a rapid paralyzing effect on the olfactory nerves, and for this reason, persons in the area were not immediately aware of the hazard.

Hydrogen sulfide has a specific gravity of 1.54 at 0° C.; the gas flows to the lowest accessible area. The hydrogen sulfide generated in and escaping from tank No. 1 flowed from the upper floor down onto the lower floor.

The events transpiring in the next several hours were reconstructed from the testimony of various survivors and persons involved in the rescue operations.

About 10:30 p.m., J. D. Langley, molybdenum flotation operator, was walking from his workbench on the lower floor toward the drinking fountain and became ill. He was having considerable difficulty breathing and was becoming nauseated. As he turned and started walking back toward his workbench to telephone for assistance, he fell unconscious. He regained consciousness in a very few minutes, probably because he fell near an open window.

He then crawled approximately 15 feet to the telephone and called the foreman's office. Don Brough was in the office with Metallurgist Dan Matthews, victim, and another man. Brough answered the telephone and left the office immediately, walking toward the molybdenum section. Arthur Sancedo, working in another section of the concentrator, had seen Langley fall and then struggle toward the telephone, and he went to that area to assist him. Upon arriving at the scene, Brough instructed Sancedo to assist Langley out of the concentrator. Brough used the moly section telephone to call the security guard for an ambulance; he also placed a call to Paul Musgrove, mill superintendent, at his residence. Brough told Musgrove something was wrong at the moly plant, but he was not sure of the problem. Musgrove, en route to the concentrator, picked up Rex Curtis, chief of security.

Dan Matthews, victim, aware something was wrong in the concentrator, went from the foreman's office down toward the moly section. As he crossed the upper floor, he passed near the three tanks and apparently suspected trouble from one of them. Evidence indicated he climbed some steps beside No. 1 tank and then fell, probably unconscious from the effect of the fumes. He apparently regained consciousness long enough to crawl approximately 20 feet to a point where he was later recovered by rescue personnel.

By this time, other persons working in nearby areas of the concentrator became aware that something was amiss in the molybdenum section. Nine persons entered the area and were either rendered unconscious or were affected to the extent that they required medical attention.

Curtis and other members of the security force had received training in the use of rescue breathing apparatus. These men, and others who had received no training, used the several pieces of available breathing apparatus to recover the affected and sometimes unconscious persons from the area.

Brough and Martinez, victims, were removed from the lower moly floor where they had lost consciousness. Reportedly, the last victim was removed from the area shortly after 12 midnight.

During the investigation, the thermostat controlling the heat supplied to the No. 1 reagent storage tank was removed and tested at the electrical shop. The thermostat had been set to turn off the heat at 155° F. The tests indicated the thermostat operated at 166° F., which was 1° more than the 10° variation which the manufacturer said could be expected, but was still below the temperature required for generation of hydrogen sulfide from a stable solution. The probe thermometer on the mixing tank was found to be accurate to within 1° C.

The 0.5 normal sulfuric acid and the phenolthalien used in the titration at the mixing tank were checked and found to be of good quality.

The small amount of reagent solution remaining in the mixing tank represented the quantity of reagent in the transfer pump line that had drained back into the mixing tank; the reagent was checked and found to be "burned". This indicated the reaction generating hydrogen sulfide and, in turn, spoiling the reagent, was occurring at the time the solution was being pumped into No. 1 tank. This reaction had, according to company personnel, occurred at other times, but the reagent had been retained at the mixing tank where the fumes were either dissipated in the open air or were exploded above the tank. Serious injury from such explosions had not occurred.

Apparently sufficient time was not allowed for the solution to become mixed thoroughly after the third partial barrel of phosphorus pentasulfide was added. For this reason, a temporarily misleading temperature was registered on the thermometer. As the solution was pumped from the mixing tank to the No. 1 storage tank, the phosphorus pentasulfide dissolved, and the temperature elevated to a point where spontaneous reaction liberating hydrogen sulfide occurred. Soon after the air had cleared, according to witnesses, the side of No. 1 tank was so hot that it could not be touched.

CAUSE OF ACCIDENT

The cause of the accident was pumping a reacting solution, generating hydrogen sulfide, into a storage tank in the concentrator. Underlying the direct cause was management's failure to provide and insist on proper procedures and proper equipment for mixing, handling, and storage of "Nokes Reagent".

RECOMMENDATIONS

Compliance with the following recommendations may prevent accidents of a similar nature:

A reacting solution should not be pumped from the mixing tank into the storage tanks. Enough time should elapse to assure that the chemical reaction has reached completion before pumping the solution from the mixing tank.

The amount of sodium hydroxide used in each reagent batch should be increased to provide a greater margin of safety.

Only experienced and well-qualified reagent mixing personnel should be used. These men should understand the chemical reactions which occur, the tests to be made, and the potential hazards involved.

An accurate method to measure reagent ingredients should be instituted.

A system should be instituted whereby the exact quantity of ingredients added by a previous shift may be known positively.

The "Nokes Reagent" storage tanks should be moved outside the concentrator building.

Hoods and exhaust fans should be installed over each of the three "Nokes Reagent" storage tanks. A method to flare or chemically absorb escaping hydrogen sulfide gas should be investigated.

The setting of the thermostat controlling the temperature of the reagent kept in the three storage tanks should be lowered.

An audible hydrogen sulfide alarm should be installed inside the concentrator.

The following recommendations have no bearing on this accident but should be complied with to prevent possible future accidents related to this reagent:

Additional lighting of an explosion-proof type should be installed in the mixing tank area. Also, all electrical equipment near the mixing tanks should be of the explosion-proof type.

Preferably phosphorus pentasulfide and sodium hydroxide should not be stored in the same building; if stored in the same building, they should be separated by a fireproof partition.

Reagent piping in the concentrator area should be color coded or otherwise identified.

The three "Nokes Reagent" storage tanks should be filled independently and not by the use of overflow pipes from one to another as reportedly was being done.

ACKNOWLEDGMENT

The cooperation and assistance of all persons participating in this investigation are gratefully acknowledged.

E. Levi Brake

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Mining Engineer

Approved:

E. A. Morgan

E. A. Morgan
Subdistrict Manager

APPENDIX A

TYPE OF INJURY	NAME	AGE	NO. OF DEPENDENTS	OCCUPATION	EXPERIENCE THIS MINE	TOTAL RELATED EXPERIENCE
Fatal	Donald L. Brough	42	3	Assistant Shift Foreman	17 years	17 years
Fatal	Richard O. Martinez	32	1	Millman	13 years	13 years
Fatal	Dan Matthews	32	3	Metallurgist	2 years	5 years
Injury	Raymon A. Smyers	45		Concentrator Shift Foreman	24 years	24 years
Injury	Francisco A. Guerra	50		Millman	19 years	21 years
Injury	J. D. Langley	45		Molybdenum Flotation Operator	25 years	25 years
Injury	Arthur F. Sancedo	36		Millman	12 years	12 years
Injury	Joe Glasco	33		Belt Laborer	2 months	8 months
Injury	James R. Roberts	34		Assistant Chief of Security	3 months	5 years
Injury	Joseph Crago	43		Security Patrolman	1 day	3 years