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FMPC POLLUTION CONTROLS
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FMPC POLLUTION CONTROLS

by

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FMPC POLLUTION CONTROLS

I. INTRODUCTION

The National Lead Company of Ohio is the contract operator of the U. S. Atomic Energy Commission Feed Materials Production Center (FMPC), located at Fernald, Ohio, about 20 miles northwest of Cincinnati.

FMPC processes uranium ore concentrates, recycle metal and other materials, by-products, etc., from uranium processing operations to produce uranium fuel element cores for use in atomic reactors. Intermediate products, principally UO_3, are also produced.

FMPC is an integrated facility, having its own water treatment plant, sewage treatment plant, fire protection system, and steam plant. Only electricity and natural gas are purchased. It cccupies an area of 1,050 acres in Hamilton and Butler counties. The production area proper is 136 acres. The cost of buildings and equipment as of now is approximately 120 million dollars.

As might be expected in such an integrated facility, FMPC could put out many possible pollutants. The power plant contains four boilers, each with a capacity of 75,000# of steam per hour. It burns coal and therefore we could have problems with particulates and SO_x.

Our processes are of both "wet" and "dry" types. Typical of our dry operations is the processing of MgF_2 slag produced as a by-product of our UF_4-magnesium metals reduction operation.

The slag must be crushed, ground, screened and otherwise processed to remove uranium and magnesium metals and produce slag liner for our reduction pots. This could obviously be a very dusty operation, and unless carefully controlled, could emit quantities of process particulates to the atmosphere. There are a number of furnacing operations which similarly could emit particulates to the atmosphere if dust collection equipment were not supplied.

The facility utilizes nitric acid in substantial quantities in its chemical processes. For example, nitric acid is employed in pickling of recycle metal to remove oxides. HNO_3 is also used in the digestion of the various concentrates and recycle materials. These operations could, unless controlled, send forth substantial quantities of NO_x into the atmosphere.

The other pollutants listed by EPA, i.e., carbon monoxide, photochemical oxidants, and hydrocarbons are of only very minor importance; however, we are alert to all possible sources.

I. AIR POLLUTANT CONTROLS AND METHODS

The recovery of internal recycle metals is a major part of FMPC operations. The aggregate amount of dusts, chips, crops and other residues generated in the many process steps is nearly equal to the net production of finished fuel cores. Because of the value of uranium metals, FMPC, long before ecology and air pollution controls became a popular subject, recovered essentially all residues. More than seventy dust collectors, scrubbers, and electrostatic precipitators are operated to prevent the loss of process particulates

into the atmosphere. Similarly, substantial equipment installations recover NO_x as dilute nitric acid and at the same time prevent the loss of NO_x to the atmosphere. Thus, over the years, FMPC has acquired a fund of knowledge of dust collection, fume scrubbing, etc., which we believe to be far superior to that possessed by most industrial installations.

Let us examine the various pollutants with reference to their controls at FMPC. As indicated earlier, we burn coal (good, low sulfur, coal) in our power plant. We have investigated various methods of controlling particulate emissions from our power plant stacks. Electrostatic precipitators were found to be perhaps feasible, but not easy to operate at the required efficiency when using low sulfur coal and certainly very expensive to install. Gas is unavailable. Present plans are to convert to No. 2 fuel oil operation.

Our dust collectors, scrubbers, and electrostatic precipitators are efficient and well maintained and, as a result, we have no particulate emission problems from our processes. A monitoring system is employed which continuously samples dust collector stacks. These samples are analyzed on a regular basis and give us complete information as to stack losses.

We use many types of dust collectors (shaker, reverse blowback, etc.). Many brand names (American Air Filter, Turner-Haws, Day, Sly, Micro-pulse, etc.) are represented in equipment installed at our site. We use many types of bags and bag materials.

Each collector is installed with bags chosen specifically for the conditions under which it is to be operated, such as dust particle size, gas temperature, etc.

We operate both venturi and high efficiency type scrubbers, mostly on furnace off-gases. Electrostatic precipitators are available to handle the ventilation of our machining facilities.

Each process and process step is examined and dust collection and ventilation systems designed specifically for each application in order to protect the health of our employees and eliminate to the maximum extent possible emission of particulates to the atmosphere. Only in this way can results such as we have achieved at FMPC be obtained. There is no all-purpose device to prevent particulate emissions.

NO_x is a pollutant which has only in recent years been recognized by the general public. Indeed, the EPA itself added NO_x to its list of pollutants in a belated fashion considerably after the original five were named. Unusual? Perhaps and perhaps not! After all, on a world-wide basis, man-made sources of NO_x produce but a <u>tenth</u> of the NO_x produced naturally. Methods of analysis for NO_x in the ambient air were not too reliable and, for that matter, are still the subject of considerable controversy today. It wasn't until proper emphasis was placed upon the fact that the distribution of man-made NO_x was closely related to population distribution, that the problem of hazardously high NO_x ambient concentrations was recognized.

Over sixty percent of the NO_x emissions in the United States occur in urban areas. Mobile sources contribute greater proportionately to the NO_x at ground level than do stack emissions. Meterological factors affect distribution. NO_x has a residence time in the atmosphere of three to four days. Thus, pollution from NO_x is a regional rather than a global problem. Thus, also, the apparent reason for EPA, and in turn the State of Ohio, establishing the Priority I classification for any region containing an area whose 1970 "urban place" population exceeds 200,000, in the absence of measured data to the contrary.

What is NO_x? Nitric oxide (NO) and nitrogen dioxide (NO_2) are generally grouped together and for convenience termed NO_x. Nitrous oxide (N_2O) at the levels emitted by most chemical processes is believed to be innocuous and is not included in the definition of NO_x. NO is a colorless, invisible gas. NO_2, on the other hand, is extremely visible, characterized by a reddish-brown color. Both NO and NO_2 can have adverse health effects but NO_2 is considerably more toxic than an equal concentration of NO. NO and NO_2 interact with hydrocarbons in the atmosphere in the presence of sunlight to generate eye irritants. In addition, the reddish color of NO_2 can contribute to haze and decreased visibility.

NO and NO_2 are generated in varying amounts by power plants, chemical processes and automobiles, plus some minor sources. Generally it is accepted that 53 percent of the man-made NO_x is generated by stationary sources, with automobiles (mobile sources) being responsible for the remainder. Of the 53 percent, less than two percent of the NO_x is emitted from chemical process sources.

In fuel burning equipment, NO is generated in the combustion process. It reacts relatively slowly with the residual oxygen in the combustion equipment and in the flue gases to yield NO_2. Because of the short residence time, this conversion is usually limited to less than ten percent and therefore NO_x in power plants is largely NO and essentially invisible.

The NO_x emissions from existing power plants are very difficult to control and at present there appears to be no acceptable abatement methods. The formation of NO is favored at high temperatures. Generally, it can be said that the more thermally efficient the combustion in a power (steam) boiler the greater the amount of NO produced. Care must be taken in combustion correction methods used to reduce NO formation lest a penalty be paid in the increased particulate matter (fly ash, unburned carbon) discharged from the stack!

Since the problem of NO_x from boiler plants is restricted mostly to the utilities with their large combustion units, we will devote most of the remainder of our discussion to the problems of removing the very small amounts (proportionally) of NO_x emitted to the atmosphere by chemical processes.

EPA (Federal) regulations establish an ambient air quality standard for NO_x as not exceeding 100 $\mu g/m^3$. Expressed differently, this is equal to .05 ppm NO_x measured as NO_2 in the ambient air. The State of Ohio in AP-7-01 establishes the same ambient air quality standard.

It might be noted at this point that repeated measurements taken at FMPC indicate that the NO_x in the ambient air at the site boundaries is less than 30% of this standard.

In prescribing for the control of nitrogen oxide emissions from stationary sources, State of Ohio Regulation AP-7-06(B) states that "all stationary nitrogen oxide emission sources shall minimize nitrogen oxide emissions by use of the latest available control techniques and operating practices in accordance with the best current technology." Thus, a chemical plant operator must ask himself, "What control techniques are available and what is the best current technology?" We at NLO have asked ourselves this question with respect to our processes. Let's look at some of the answers we have developed.

When nitric acid is used to dissolve oxides from metals (pickling), NO_x is formed and must be vented from the process to protect the health of employees in the area. Usually NO_2 is predominant and therefore the stack gas forms a characteristic reddish-brown plume. Since most pickling facilities are "batch" operations the emissions are sporadic and variable.

Scrubbing the NO_x fumes using normal or accepted equipment such as venturi or packed tower type scrubbers is ineffective. NO_2 is not readily absorbed by water (as compared to some other fumes such as ammonia, etc.) and NO is classified as essentially insoluble. We at NLO have investigated the use of various additives to the

scrubbing solution to increase the scrubbing efficiency. Caustic, permanganate, and urea additives have been of little or no benefit in these types of equipment.

More radical approaches to the problem were obviously necessary. The addition of urea directly in the nitric acid pickling solution was tested. At first, dry granular urea was added in various concentrations. The result was an almost total absence of NO_x fumes. After a lengthy test period an optimum concentration of urea in the nitric acid bath was developed. Equipment was then installed to add metered amounts of concentrated urea solution to the bath and thus maintain the desired urea concentration during the pickling operation. The urea addition method is so effective that we now employ it in all small batch digestion and metal pickling and dissolution operations.

Work is still going on to improve a minor and yet the only significant defect in the method. During transfer of the pickled metal from the pickling bath to the rinse, the urea in the pickle solution remaining on the metal is apparently consumed and NO_x evolution commences. The transfer must be made very rapidly to prevent emission of the small amounts of NO_x which could evolve.

At FMPC we also have several processes which are capable of generating such large quantities of NO_x that when the facility was originally constructed, equipment was installed to handle these fumes in such a manner that not only was air pollution reduced and our employees' health protected, but also the NO_x was converted to dilute nitric acid for re-use in the production processes.

The metal dissolver, one of these processes, is used as its name suggests, for the dissolution of recycle uranium metal in nitric acid. The product is uranyl nitrate which is returned to the product stream. During the dissolution step NO_x is produced, the quantity and rate dependent upon acid concentration, quality and quantity of metal being dissolved, and the manner of dissolution.

As the final step in the manufacture of UO_3 (an orange powder), pure uranyl nitrate (a liquid) is heated and is denitrated in large kettles or denitration pots. In the process, NO_x is driven off. A portion of the NO_x is recovered by individual pot scrubbers. The remainder of the NO_x is sent, along with the NO_x from the metal dissolver, to the absorbers in the nitric acid recovery area.

The function of the absorber is similar to that of a scrubber in that NO_x is removed from the gas stream by absorption or reaction with water; however, it is at this point that the similarity ends. An FMPC absorber looks like a cylindrical stainless steel tower, 8 feet in diameter and approximately 64 feet high. Inside the tower are 27 bubble cap trays spaced two feet apart. The absorber scrubbing medium (water at the beginning) enters the tower at the top and flows downward through the tower. Each tray retains 2-3/4" - 4" depth of liquid. Piercing and projecting upward from the bottom of each tray are sixty-five 3½" diameter nipples, each topped with a 6" bubble cap. The NO_x off-gas enters near the bottom of the absorber under pressure and in order to proceed upwards and through the absorber it passes through the tray nipples

and is deflected by the bubble caps through the liquid retained on the tray. Since there are 27 trays, it could be said that each absorber consists of 27 scrubbers in series. The absorber can be more effective than a simple scrubber and in addition returns the scrubbing medium from the bottom of the absorber as dilute HNO_3 for re-use.

FMPC employs two absorbers in series, i.e., the gas flow proceeds directly through the second absorber after discharge from the first. The off-gas from the second absorber, with most of the NO_x removed, passes to a tall stack, from which it is discharged 104 feet above ground level.

The operation of the absorbers is carefully controlled to insure maximum removal of NO_x from the off-gas. The entire system is monitored by a Model 461 duPont NO_x analyzer system which samples the gas stream at four points, analyzes NO and NO_2 concentrations of each sample, and records the analytical data. It requires five minutes for each sample analysis so that each point is checked and recorded every twenty minutes. This monitoring system cost approximately $26,000. At the present time we are reviewing the possibility of using the system to fully automate absorber control and operation.

We at NLO feel that we are doing a good job of reducing the NO_x emissions from the absorbers but the State of Ohio regulations, if taken literally, say that we must use the "latest available control techniques and operating practices in accordance with best current technology." The question then is, "Are there better available

control techniques which we could apply to our absorbers?" Actually we have continuously sought answers to this question since the start of operations at FMPC. Thus we were knowledgeable about most techniques of absorber operation when, approximately three years ago with the advent of air pollution controls, the need for up-to-date answers became evident. Let's discuss some of the techniques we have examined and changes we have made.

As originally installed, the two absorbers at FMPC operated in parallel, i.e., each absorber handled half of the gas stream. Results of a number of tests indicated that NO_x absorption efficiency could be increased by operation of the towers in series, thus taking advantage of longer gas travel and increased time of exposure to the absorbing medium. The necessary modifications to ductwork, piping, and pumps were made, and, as indicated earlier, the series mode of operation is presently employed.

As with the other scrubbers, we investigated the use of various additives in the scrubbing medium in the absorber towers. We tested the use of caustic (NaOH) in one absorber while continuing water in the other absorber, operating the absorbers in parallel. The caustic was slightly more effective in NO_2 removal, but no significant increase in efficiency of absorption of NO was found. Moreover, the use of caustic was not particularly attractive since it appeared that we would be trading an air pollution problem for a water pollution problem in the disposal of the sodium nitrate solution formed.

Urea was added in the absorber liquid. Essentially no improvement in NO_x absorption was found. A more sophisticated use of urea, using it in combination with 2-3 N HNO_3 at elevated scrubbing solution temperatures was tested in the second absorber with the absorbers in series operation. Here, no significant reduction of NO_2 was caused; however, the urea was more effective in the removal of NO. Unfortunately, this wouldn't even help the cosmetic problem, since the color of the stack plume would be essentially unchanged.

In none of the tests involving additives to the absorber liquid was sufficient improvement realized to warrant continuation of their use. Attention thereupon was turned to possible benefits to be derived from installation of equipment to treat the tailgas from our absorbers. The John Zink Company and Universal Oil Products Company (UOP) offer an incineration technique. At first glance the technique appears attractive; however, in our operations with intermittent variations and even cessations of NO_x flow, it became evident that the burning of the large quantities of natural gas (if such were available) in the NO_x incineration process would probably cause more air pollution from the products of combustion than we are now putting out with the NO_x. Also, unless very carefully designed and operated, incineration may only reduce the NO_2 in the off-gas stream to NO, thus in effect, making the NO_x stream invisible without materially reducing the NO_x content.

Catalytic reduction of the NO_x to N_2 was investigated. This method has been used on the tailgas from nitric acid manufacturing plants. Our investigations show that catalytic reduction was not feasible on our off-gas stream because of the excess air in it. The oxygen in the excess air must be destroyed before the off-gas stream enters the catalytic reduction chamber. Again, very substantial amounts of natural gas or propane would be required and their products of combustion vented to the atmosphere.

One of the most promising processes presently being developed employs molecular sieves. In this process the NO_x is retained in the molecular sieve material like a sponge absorbing water. The off-gas, less most of the NO_x it formerly contained after passing through the molecular sieves, is then vented to the atmosphere. Difficulty arises when the molecular sieve material has absorbed NO_x to its full capability and must be regenerated. The regeneration operation requires that at least a pair of molecular sieve towers or chambers be installed so that absorption capacity is available for process use in one unit while the molecular sieves in the second are regenerated. The regeneration process, accomplished by forcing heated air (600°F) through the molecular sieve material, removes the contained NO_x in the form of HNO_3 and NO_2. The HNO_3 and NO_2 gas is passed through a condenser and an absorber (similar to the type used at FMPC but pressurized) where the nitrate values are recovered as relatively concentrated nitric acid. The tailgas from the absorber is returned to the second (on-line) molecular sieve chamber for reabsorption of any remaining NO_x.

The advantages of the molecular sieve process are:

1. Nitric acid is recovered in usable concentrations, thus improving the economics of the NO_x pollution control operation.

2. Relatively small amounts of fuel and power are required (as compared with systems such as incineration).

3. The system is relatively indifferent to variations in NO_x concentrations in the off-gas being processed, and no major problems are anticipated with intermittent off-gas flows.

The prime disadvantage is very high initial capital cost, since stainless steel is the principal construction material. Precise control instrumentation is required. Similarly, maintenance could be costly since corrosion promises to be a problem. Nevertheless, both the Norton Company and Union Carbide (Linde Division) are working very hard on the molecular sieve concept and isolated pilot plants and even small preliminary production process units are being built. It appears, however, that it will be at least several years before the "bugs" will be removed and the system available in refined form for general use. We at NLO are watching its development very closely.

We are also working on a companion molecular sieve system which utilizes the reaction of ammonia and NO_x in the presence of molecular sieve material heated to temperatures of 300°C.

In this process it is believed the NH_3 and NO_x react to form NH_4NO_3 (ammonium nitrate) which is deposited as a powder on the heated zeolite bed. The bed in turn breaks down the ammonium nitrate and discharges from the stack N_2 and N_2O. N_2O, of course, is not believed to be a pollutant. The advantage of this system is that regeneration of the molecular sieve material is not required. It is primarily an NO_x destruction mechanism, however, and there is no recovery of nitric acid to offset operation costs. But the work is still in the laboratory stage and much remains to be done before a viable process is developed.

It should be quite obvious by now that reduction of NO_x emissions is not a simple job. The report of the National Academy of Engineering and the National Research Council entitled "Abatement of Nitrogen Emissions from Stationary Sources," issued in 1972, makes this quite clear. If this report is available to you, it would be worth your time to read it.

Under the circumstances, how are you going to know if we, or anyone else, are doing a good job of NO_x emission reduction? To answer my own question, it's not going to be easy!

State of Ohio Regulations AP-3-07 prescribe a Ringelmann No. 1 or 20% opacity as the darkest plume permissible. Judging the effectiveness of NO_x removal by the Ringelmann shade of the stack plume could be quite difficult, and in many cases could be most misleading. Let me illustrate. As I stated earlier, NO is invisible. A process discharging large quantities of NO could

not be detected at all by Ringelmann shade. Witness the lack of color in a boiler stack which probably is discharging very substantial quantities of NO. The opacity of the plume from a stack discharging NO_x is to a very major extent dependent upon the size of the stack. For instance, our stack is 42" in diameter. We have computed that in order for that plume to be invisible we would have to reduce the stack gas NO_x concentration calculated as NO_2 to less than 60 ppm. This is substantially below the ppm permissible for a new nitric acid manufacturing plant under the EPA regulations. A smaller stack could discharge substantially greater concentrations of NO_x and yet you would not detect anything amiss from the Ringelmann test.

What about sampling? We have an NO_x (and particulates) stack sampler. It cost us $2500. However, it isn't a monitor and it merely allows us to determine the NO_x concentration at that particular point of time. There are no practical isokinetic continuous samplers available for application to power plant stacks.

With respect to monitoring of NO_x discharges, as indicated previously we have invested more than $26,000 in one such piece of equipment. NO_x is relatively corrosive. We have, and expect to continue to have, high maintenance costs on this monitor. Inleakage in the sample lines or connections can give erroneous results. Considerable knowledge of operations and techniques is required to appraise intelligently the results furnished by the monitoring equipment.

In conclusion, I hope I have shed a little light on our activities at the U. S. Atomic Energy Commission Feed Materials Production Center and on the problems of NO_x abatement. We don't have all the answers; so far as we can tell, neither does anyone else. We are just trying to stay one step ahead of the rest.