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SYMPOSIUM ON IODINE PROBLEM

By

O. F. Hill, et al

August 3, 1955

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A symposium on the iodine problem was held in the 2704-Z Conference Room at 1:00 P.M., August 3, 1955. Papers were presented on different aspects of this problem, as known at that time, by personnel from the Radiological Sciences, Manufacturing, and Engineering Departments. Each of the speakers prepared abstracts of these papers, and these are published here for the record.

IODINE CONTAMINATION OF HANFORD ENVIRONS - J. M. Smith

The principal hazard of iodine release to the environs arises from deposition on vegetation and subsequent ingestion by animals and humans.

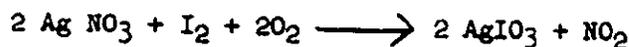
The provisional vegetation contamination limit of 10^{-5} μc I^{131} per gram of material has been shown by experiment to be safe for grazing animals such as sheep. The permissible limit for humans is based on an allowable weekly dose of 30 mrem to the thyroid gland, and permits a daily intake of \sim six μc . With vegetation levels of 10^{-5} $\mu\text{c}/\text{gm}$, this permits a daily intake of two quarts of cow's milk or about 1 1/3 pounds of garden produce. Raising the vegetation limit by a factor of ten would reduce permissible food intake quantities to an unreasonable amount.

The vegetation contamination found by experience at Hanford over the past several years was related to the amounts of I^{131} released. It was evident that, to keep the environs vegetation to the proposed limit, the daily I^{131} release must be restricted to the order of one curie. A minor variation of this was the more recently proposed ten curies per week with not more than three curies per day.

The 1955 record indicates many periods exceeding the recommendations, with resultant contamination of large areas off the project. The major difficulties involved significant quantities released from the middle of February to the middle of April. Since then the limits have been exceeded to a lesser degree, and the above limits areas receded to within the project boundaries.

SUMMARY OF THE CHEMISTRY OF THE SILVER REACTOR - G. B. Barton

The chemistry of the reaction between silver nitrate and iodine is being studied in some detail. First experiments were directed toward determination of the stoichiometry since it was postulated the reaction did not follow the equation written in the Process Manuals. Two equations can be written:



These can be combined in various proportions to give an infinite variety of product ratios. Experiments in the laboratory have indicated a wide range of product proportions as shown by measurement of the iodide to iodate ratio.

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Pure oxygen increases the proportion of iodate over that formed in air or nitrogen. When the gaseous products are evolved into a vacuum, there appears only NO_2 and the ratio is $2\text{I}/\text{IO}_3$.

Thermodynamic calculations based on the above two equations would predict silver iodide to be the stable compound at plant operating temperature and that increasing the NO_2 concentration of the gas stream would result in an iodine loss. Experiments have shown that NO_2 will displace iodine from the reaction mixture or prevent its initial absorption, but silver iodide is not the only product.

The passage of ammonia may result in the transport of iodine from the reactor as very finely divided particles of silver iodide-silver nitrate formed when the gaseous products of ammonia reduction of silver nitrate cause the liquid to bubble. This reaction goes vigorously at 190 C. At lower temperatures, the reaction is not vigorous enough to cause appreciable iodine transport.

The present state of our knowledge of the reaction between silver nitrate and iodine indicates it cannot be treated in a straightforward fashion, either stoichiometrically or thermodynamically.

OBSERVATIONS ON THE EVOLUTION OF IODINE AT "T" PLANT - G. L. Helgeson

The contributions of the sand filter effluent gases and the three dissolver off-gas streams to the total iodine emissions from the T Plant stack were carefully studied for the period from April 1, 1955, through May 27, 1955, through the use of data obtained from 1034 caustic scrubber samples. The sand filter gases contribute an average of 0.18 curies per day. It is generally agreed that this is in keeping with present production schedules and cooling time. One can deduce, however, that with present production conditions it will be exceedingly difficult to limit the total iodine emissions to 0.3 curies per day. The 3-5L system is seen to be the least offender, with an average daily emission of 0.17 curies, with 79 per cent emitted during dissolving operations and 21 per cent during other periods. The average daily emission from the 4-5L system was 0.27 curies, with 59 per cent emitted during dissolving operations and 41 per cent during other periods. It is obvious that the 3-5R system has been the major source of iodine emissions during the entire sampling period, with an average daily emission of 0.60 curies. It is also seen that 78 per cent of the emissions occurred during periods other than dissolving, such as charging, coating removal, or standby. Likewise, it is of interest to note that emissions during periods other than dissolving fell off sharply after May 19, 1955, on which date "it was agreed that the heater Micromax to the silver reactor inlet should be lowered from 375 F to 355 F".

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EXPERIMENTAL STUDIES ON THE EVOLUTION OF IODINE AT "T" PLANT - W. C. Schmidt

In addition to the routine samples of dissolver off-gas taken just prior to the entrance to the stack, several special samples were drawn from individual pieces of equipment in the dissolver cells. Each time a sampling period was started, three simultaneous samples at the same flow rate (0.5 cfm) were drawn through three liters of 33 per cent sodium hydroxide solution.

One of these samples was taken on May 13, 1955, from the 3-5R off-gas system when the 50 foot level stack monitor indicated a severe iodine emission was occurring. During a 40 minute sampling period, 1.3 curies of radio-iodine were found leaving the off-gas filter, 2.0 curies were found entering the filter, and .06 curies were found leaving the dissolver vessel. The estimated emission from this dissolver was eight curies over a six hour period. The dissolver was being held at 25 C in sodium nitrate solution during this evolution.

- * Two different samples indicated that radio-iodine was being released during coating removal. On May 2, 1955, the samples indicated that 0.09 curies were being evolved from the dissolver vessel, 0.25 curies were leaving the silver reactor, and 0.2 curies were passing the filter. Again on May 19, 1955, the samples showed 0.03 curies leaving the dissolver vessel, 3.88 curies were leaving the silver reactor, and 4.23 curies were passing the filter.

ADDITIONAL OBSERVATIONS ON THE EVOLUTION OF IODINE AT "T" PLANT - W. G. Browne

A graph of the T Plant I^{131} emissions was presented, and several observations were discussed.

1. The emission problem at T Plant became more serious after a month of low level uranium dissolution than it was under shorter cooled high level uranium dissolution.
2. As production schedules went up, I^{131} emissions tended to increase and become more erratic, but not as a direct function of increased dissolving.
3. Although there seems to be some change in I^{131} emissions as cooling times for the uranium become shorter, a change back to longer cooling times did not correct the problem as had been anticipated.
4. The use of 50 per cent nitric acid for starting the uranium dissolution reaction instead of 60 per cent nitric acid seems to minimize the I^{131} emissions which occur during the dissolving cycle.
5. Some serious and erratic emissions of I^{131} occur when the dissolver is holding in sodium nitrate solution or at the start of the coating removal step.

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6. A study of the data indicates the possibility of the I^{131} emissions being in two forms, gaseous or particulate.

Three charts were shown which showed I^{131} emissions as recorded by the 50 foot level stack sampling and absorption column system, monitor.

1. An emission which occurred during replacement of the 3-5R filter.
2. An emission which occurred during coating removal in the 3-5R dissolver. Off-gas line Beckman monitor readings for each dissolver, corresponding to the emission, are also plotted on the same chart.
3. An emission from the 3-5L dissolver system showing a good correlation between the off-gas line monitor readings and the 50 foot level monitor. This chart shows why we have confidence than an instrument such as the gamma scintillation monitor can be devised which will indicate instantly when an I^{131} emission is starting.

OBSERVATIONS ON THE EVOLUTION OF IODINE AT REDOX - A. J. Waligura

Prior to February, 1955, a reasonable control of iodine from the Redox processes was met. Instances of iodine emissions in the order of two to three curies occurred periodically and were corrected by regenerating the silver reactors. During February of 1955, while processing low exposure metal cooled 76-88 days, iodine emissions of four to six curies per day occurred. At this time, mercuric nitrate in the concentration of 1.05×10^{-3} M Hg was added to each cut prior to dissolution to inhibit the evolution of iodine. A ten-fold reduction in iodine was achieved, but conclusions were confused by sporadic bursts which occurred despite use of the Hg^{++} . During use of Hg^{++} , the amount of iodine detected in the process air leaving the sand filter became significant (ca. 0.4-0.6 c/day). For this reason, use of Hg^{++} on a routine basis is not desirable.

Initial work with the sampling equipment of the individual gas stream confirmed previous experience wherein the peak iodine emission in the Redox process appeared to occur near the start of the second cut. By reducing the concentration of the initial acid of the second cut from 49 per cent to 39 per cent, an appreciable reduction in the peak emission was achieved, but, from a study of the data, it would appear that no major improvement in iodine control may be expected from procedural changes.

Samples of the dissolver during coating removal have shown that the amount of iodine released during coating removal is relatively small as compared to that given off during cuts. However, it appears that with ~97 day old metal, the amount becomes appreciable, and indications are that bypassing the reactor on a routine basis during coating removal may not be desirable.

In July, instances of iodine emissions from the C-3 reactor during holding in nitrate or start of coating removal period arose. Individual gas samples taken during these periods disclosed the following data.

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1. Iodine content of the reactor effluent gases was at least 50 fold higher than the concentration in the influent gases.
2. Iodine activity in the dissolver off-gases was approximately 100 fold higher than hitherto found during this operational step.
3. An apparent decontamination factor of eight was being demonstrated by the in-cell filter.

EXPERIMENTAL STUDIES ON THE PERFORMANCE OF A BACK-UP SILVER REACTOR - K. L. Adler

Iodine retention efficiency in excess of 98 per cent was demonstrated in two runs in the bench scale back-up silver reactor in T Plant. This reactor is approximately 1.5 inches in diameter and three feet long and is packed with silver nitrate coated, one-half inch Berl saddles. Off-gas from the cell 3-5R silver reactor was drawn through the reactor at a superficial velocity of approximately one fps during metal dissolving operations. Gas temperature ranged from 182 to 191 C at the reactor entrance and from 177 to 207 C at the outlet. Samples of the gas were passed through caustic scrubber bottles both upstream and downstream of the reactor. Since the radio-iodine concentration in the downstream caustic scrubber always was less than the lower analytical limit (4×10^{-4} μ c/ml by gamma spectrometer), only minimum efficiency could be determined.

A GAMMA SCINTILLATION IODINE MONITOR - W. N. Carson, Jr.

The gamma scintillation iodine monitor is designed to utilize counting of the gamma photons emitted by I^{131} in gas samples. The circuits of the monitor make correction for background and for the presence of ruthenium and krypton in the sample. The sensitivity is estimated to be about 0.06 curies per day for Purex dissolver off-gas. Advantages of the monitor are: rapid response to changes of activity in the gas, simple sampling equipment, insensitivity of the instrumentation to changes in flow rates, and ease of absolute calibration.

DESIGN PROGRAM ON ADDITIONAL IODINE CONTROL AT SEPARATIONS PLANTS - W. M. Harty

Design reviewed its program for additional iodine control at separations plants. The status of each item of design was presented, including flowsheet, layout, feasibility, cost, and timing considerations. Topics presented included:

1. Scope designs for continuous iodine monitors (caustic scrubbing) for Redox.
2. Scope designs for continuous iodine monitors (caustic scrubbing) for Purex.

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3. Scope designs for dissolver off-gas stubs at Purex for future addition of back-up iodine facilities.
 4. Scope designs for caustic scrubbing and heater-silver reactor facilities for vessel vent, condenser vent, and inert gas vent systems at Redox.
 5. Scope designs for NH_3 scrubbers in Redox dissolver cells.
 6. Scope designs for heater-silver reactor, in-cell systems for Redox dissolver cells.
 7. Scope designs for caustic scrubbing and heater-silver reactor back-up facilities for dissolver off-gas at Redox, located in an outside of Redox facility.
 8. Scope designs for acid recovery from dissolver off-gases at Redox, located in an outside of Redox facility.
 9. Scope designs for NH_3 scrubbers at Purex.
 10. Scope designs for a heater-silver reactor system for in-cell treatment of Purex vessel vent gases (backing up existing heater-silver reactor system).
 11. Scope designs of heater-silver reactor back-up facilities in Purex dissolver cells, including:
 - (a) Heater-silver reactor-silver reactor system with side by side reactors.
 - (b) Heater-silver reactor-silver reactor system with stacked reactors.
 - (c) Heater-silver reactor-heater-silver reactor system with stacked heater and side by side reactors.
 12. Scope designs for a heater-silver reactor system for Purex dissolver off-gases, located in an outside of Purex facility.

The proposed future design scoping program was outlined.

NEW INFORMATION

Since the symposium, several additional pertinent observations have been noted. These are included here for completeness of the status of the iodine problem as it stands at publication time.

1. At T Plant, the 3-5R and 3-5L heater-reactor systems were operated in series. The following conclusions were drawn:

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- (a) The 3-5L reactor (acting as "back-up" reactor) operated at >> 98 per cent efficiency under all conditions.
 - (b) With an increase in the inlet temperature between 300 F and 400 F, the efficiency of removal decreases during coating removal and the efficiency of removal increases during dissolving steps.
2. Sodium nitrate used during coating removal and periods of holding metal heels has been found to contain significant amounts of iodate. It is postulated that nitric acid leaking into the dissolvers reacts with the metal heel, reducing the iodate to liberate I^{127} , which then displaces I^{131} from the reactor. At Redox, careful control of acid leakage into the dissolvers, plus the precautionary addition of sodium hydroxide with the sodium nitrate to the metal heels, appears to have prevented this type of emission.



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