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# THE RELEASE AND ADSORPTION OF METHYL IODIDE IN THE HFIR MAXIMUM CREDIBLE ACCIDENT

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## ABSTRACT

This study was undertaken to establish both the maximum percentage of the iodine inventory which could exist in the containment vessel as methyl iodide, and the efficiency of the HFIR-SBHE system filter for methyl iodide. Review of all known existing relevant data has led to the conclusion that 5% of the iodine is the upper limit which can exist as $CH_3I$. The removal efficiency of Barnebey-Cheney Type 513 coconut charcoal heretofore proposed for use in the HFIR filters was determined for a number of conditions of humidity, flow rate, flow time, and bed depth. At the 70% relative humidity, the removal efficiency of 1-in. charcoal, 50 $ft^3$ $min^{-1}$ flow is only 85% after two hours and decreases with continued flow time. Under similar conditions, MSA-85851 charcoal - an activated impregnated coconut charcoal - has an efficiency of 92% after 28 hours. Although investigation of methyl iodide absorption on charcoal is still continuing, it is recommended that the HFIR filter employ a 2-in. bed of the MSA charcoal.

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# 1. INTRODUCTION

The High Flux Isotope Reactor, HFIR, is a 100 MWT experimental reactor located at the Oak Ridge National Laboratory.[1] Its containment consists, in part, of a concrete hall which is continuously vented by a forced draft system which discharges to a 250 ft stack. The safeguards analysis of the facility[2] presumes that the filters in the off-gas system will at all times have a particulate decontamination factor (as demonstrated by a DOP test) of at least 1000 (99.9% removal efficiency) and an iodine decontamination factor of 667 (99.85% removal efficiency). It is the purpose of this memo, first to define the fraction of iodine which is released from the primary system as methyl iodide, and second to establish the efficiency of the filter system for methyl iodide during the HFIR accident conditions. In addition, consideration is given to design, installation and periodic test provisions which we believe will be required for the filter system to be acceptable to AEC regulatory authorities as an adequate engineered safeguard.

While the use of filters in off-gas systems is common practice in the nuclear industry, their use as accepted engineered safeguards in reactor installations has been somewhat limited to date. In fact, their principal use in this regard has been on Commission-owned facilities, e.g., NS Savannah,[3] ORR,[4] NPR,[5] EGCR,[6] etc., where with the exception of the NS Savannah the siting requirements were not

as stringent as for most licensed power production facilities. The filter system in the facilities almost invariably provided for the removal of both particulates and elemental iodine in different trapping devices. However, recent experimental work both in the United Kingdom and the United States has demonstrated that some small fraction of the released iodine is frequently in the form of methyl iodide ($CH_3I$). Furthermore, the removal efficiency of iodine filters is generally lower for methyl iodide than for elemental iodine, and the efficiency for methyl iodide is also known to be quite sensitive to the moisture content of the gas. Thus, the problem of attaining a given iodine removal efficiency involves first the determination of the most unfavorable distribution of the released iodine between elemental iodine and methyl iodide, and second, the determination of the removal efficiencies of the filter system for these constituents under the accident conditions.

It should be noted that this discussion has not specifically considered iodine on particulates or iodides other than methyl iodide. This is justified since not only are these forms of iodine produced in relatively small amounts, but a filter system designed to remove particulates, elemental iodine and methyl iodide would have better removal efficiencies for these other forms of iodine. Furthermore, the removal of iodine from a dispersion by bubbling through water is not further considered here both because of the inability to determine what the bubble size would be and because of the

paucity of experimental data on the removal of iodine from such bubbles. Such relevant data as do exist, however, indicate that the solubility of iodine in water is low[7,8] and that methyl iodide is not readily removed from the dispersion.[9]

As background for consideration of the question of methyl iodide formation and filtration, this memo will first summarize the description of both the HFIR Maximum Credible Accident and the HFIR Dynamic Containment System as taken from the HFIR safeguard[2] and design reports.[1] Relevant experience with methyl iodide is then presented in the following two sections leading up to the discussion and recommendation at the end of this report.

## 2. THE HFIR MAXIMUM CREDIBLE ACCIDENT (MCA)[1,2]

Despite the arguments presented in the HFIR safeguards analyses to show that the potential accidents are either very unlikely or have been recognized and precautions taken to prevent them, there still exists the finite probability that a fission product release may occur. Such a release may be the result of minor damage to the fuel with insignificant results or may consist of an extensive meltdown of the core accompanied by a release of a substantial fraction of the fission products. Paradoxically, the accidents which are most likely to result in extensive damage to the reactor internals and cause large fission product release from the

fuel can occur only under conditions of double containment, and if the primary containment remains intact, there will be little or no release of fission products to the atmosphere. On the other hand, fission product releases which occur when the primary containment is inoperative will be of lesser magnitude, but will be discharged through the Special Building Hot Exhaust (SBHE) system and cause some environmental contamination.

The potentially worst case would involve extensive meltdown of the core concurrent with failure of the primary containment. This is considered highly improbable, because of the strength of the primary system and because a depressurization accident caused by rupture of the primary coolant system would not result in extensive melting. Nevertheless, to cover any such possibility, the MCA is postulated to be an extensive meltdown of the reactor core concurrent with a failure of the primary containment sufficiently severe to allow some of the fission products to escape directly into the building, but not violent enough to grossly rupture the reactor vessel or the high pressure piping.

In order to obtain a realistic estimate of the consequences of the MCA, it is first necessary to establish the amount of fuel which could sensibly be considered to be involved. In the worst accident heretofore, the SL-1 accident, ~ 32% of the core was melted with ~ 50% of the fuel reaching melting temperature. In the SPERT-I

destructive test about 35% of the core was melted.[10] In the calculations presented in the safeguards report,[2] it is estimated that at worst 24% of the core could melt. On the basis of this information, it seems reasonable to postulate that the MCA will involve no more than 50% of the fuel plates. It will be further assumed that 50% of the iodines, 100% of the noble gases, and 2% of the other fission products present following 15 days operation at 100Mw, would escape from the immediate vicinity of the affected portion of the fuel. These fractions are in agreement with current practice and appear to represent reasonably realistic, but still conservative, estimates, although the fraction chosen for the solids is somewhat higher than that usually recommended.[11]

Two cases can be distinguished: first, where the release takes place within the primary containment system with the concurrent release of a large amount of energy from a power excursion or chemical reactions (this case is not considered further here) and, second, where the meltdown occurs outside the primary containment. In the latter case, because the mechanisms available to initiate melting are somewhat less potent than those which could cause an accident at full power, it is not anticipated that any sizeable energy release would occur; and quite probably the fission product release would be less than that postulated. Moreover, except for the case of meltdown of a spent fuel element as a result of afterheat, virtually all of the overheating accidents outside the primary containment would involve new fuel

elements which contain small amounts of fission products. Nevertheless, the 50% meltdown with the fractional releases previously indicated was assumed.

This is the accident of most interest with respect to environmental safety. The consequences of a 50% meltdown with the fission products discharged to the atmosphere through the SBHE system have been calculated. The only significant contributions to either the internal or external doses are from the iodines and noble gases. Assuming iodine and particulate decontamination factors of 2000 and 4500 respectively, as discussed in the following section, the maximum internal dose following infinite exposure to the thyroid due to iodine is 5.2 rem, and the maximum external dose due to noble gases is about 89 rad including both beta and gamma radiation. These both occur at a distance of about 0.8 km from the stack -- well within the site boundary. At the boundary of the controlled area, 2.82 km from the stack, these doses for infinite exposure are 2.8 rem, and 24 rad, respectively.

## 3. THE HFIR DYNAMIC CONTAINMENT SYSTEM[1,2]

The so-called "Dynamic Containment System" is the system which controls the activity which is released from the primary reactor system in the event of a MCA. Air is constantly exhausted from the several building areas and from the region directly over the pools by the SBHE. This

system, designed to remove ~ 28,600 $ft^3$ of air per minute, directs the exhaust through appropriate filters to the 250-ft HFIR stack. It provides constant inleakage of air to the potentially contaminated areas, thus preventing the diffusion of air or vapor-borne fission products from the building at ground level. The effluent air, in passing through the SBHE filters, deposits therein, with the exception of the noble gases, virtually all of its activity. Of the 28,600 $ft^3$ $min^{-1}$ exhausted from the building, 12,500 $ft^3$ $min^{-1}$ is exhausted from reactor bay area which contains reactor piping. Of this 12,500 $ft^3$ $min^{-1}$, 5000 $ft^3$ $min^{-1}$ is exhausted from inlet registers located under the plastic pool cover. Thus, for those cases where the pool cover remains in place, a third line of containment is operative.

The secondary, or building containment is required to provide protection only under the following conditions: (1) where a fission product or other release occurs while the reactor vessel is open, (2) as a result of an accident to a fuel element or to the target while they are being handled or stored outside the reactor vessel, (3) because of an accident involving an experiment or other source of radioactive material not contained in the primary coolant loop, or (4) in the extremely unlikely event of a rupture in the primary coolant system concurrent with a fission product release within the reactor vessel. Nevertheless, the secondary containment is a maximum reliability system

which is capable of handling any credible accident and which will always be in operation whenever there is a possibility of any significant release of radioactivity. Administrative safeguards require that the secondary containment be in operation whenever the reactor is operating or when fuel is being handled. Normally, the system will only be shut down when this is required for maintenance or testing. During such periods, special procedural safeguards will be effective in preventing reactor startup and fuel handling accidents.

The design criteria specify that the filter systems be capable of retaining 99.95% of all the elemental iodine. As a practical matter, every effort will be made to achieve the highest decontamination factors consistent with safety and economy. The filters will be tested following installation and periodically thereafter.

Although the filter installation is intended to meet the above criteria, laboratory-scale investigations with filter systems using these media indicate that over-all decontamination factors up to 3000 for iodine can be achieved.[12] A full-size filter system similar to, but somewhat less elaborate than, that of the HFIR has been tested in the Oak Ridge Research Reactor, and in these tests a decontamination factor of approximately 600[13] was demonstrated. Because in any such accident the iodine is released under water and must be conveyed first through the water and then through the SBHE ducts before reaching the filters, it is estimated that the amount of iodine actually

reaching the filters will be reduced by a factor of at least 3. Thus it would appear conservative to assume an over-all decontamination factor for iodine of 2000. This, as is shown in the safeguards analyses,[2] is higher by a factor of 100 than that necessary to satisfy the limits established by 10 CFR 100 under MCA conditions.

Experience has shown that the mobility of the non-volatile fission products is less than that of the iodines, that the filters will be more effective in removing them, and that they will be more effectively retained in the water and on the various surfaces. It is conservative to assume that both filtration and retention in the building will each be at least 50% more effective in the case of the nonvolatile fission products than in the case of the iodines. Consequently an overall decontamination factor of 4500 is assumed for the nonvolatile fission products.

The assumptions made regarding decontamination are summarized in Table 1.

Table 1. HFIR Decontamination Factors

| | Fraction Released From Fuel | Fraction Escaping Deposition | Fraction Escaping Filter | Decontamination Factor |
|---|---|---|---|---|
| Iodines | 0.5 | 0.333 | .0015 | 2000 |
| Noble Gases | 1.0 | 1.0 | 1.0 | 1 |
| Non-Volatiles | 0.02 | 0.222 | .001 | 4500 |

The dynamic containment system has two main branches both of which discharge into the 250-ft stack. Each branch contains an identical filter system designed to remove both particulate and volatile contaminants. The filters are located in a filter pit which contains three filter cells in parallel. The two branches of the system are each served by a separate cell. The third (central) cell serves as a standby filter system which can be put into service on either branch without necessitating a plant shutdown. Each filter cell contains an assembly of (1) a bank of 12 Fiberglas pre-filters mounted in a 3 x 4 array; (2) a 3 x 4 bank of 12 Fiberglas absolute filters; (3) a silver-plated copper mesh filter; (4) two 3 x 4 banks of 12 charcoal absorption units; and (5) a 3 x 4 bank of absolute filters.

## 4. RELEVANT EXPERIENCE ON THE FRACTION OF IODINE CONVERTED TO METHYL IODIDE IN A REACTOR ACCIDENT

### 4.1 Introduction

Fission product radioiodine invariably has been found to contain a small fraction which exhibited "penetrating" characteristics.[14] The work of Atkins and Eggleton[15] positively identified this material as a mixture of organic compounds, the major component of which, and most penetrating to a charcoal filter, was methyl iodide.

Various techniques have since been developed which lead to an assessment of the fraction of the iodine appearing in this form. The method first and most generally employed is based on the fractional penetration of a system of filter papers and metallic screens in an assembly which derived its name from the inventor, Fred May, of the UKAEA. Unfortunately, this device is subject to many ambiguities as has been pointed out by Collins[16] and others, and auxiliary devices had to be relied upon to correct the interpretation of the May Pack. Invariably the apparent value of the methyl iodide fraction is high by a factor of 2 to 10 when compared to a dilute-stream diffusion tube analysis[18] or a gas chromatographic analysis.[17]

## 4.2 Origin of Methyl Iodide in Reactor Accidents

Collins[19] has discussed a wide variety of conditions leading to methyl iodide production in a reactor accident. The two most important of these are:

1. Direct release or generation of methyl iodide from the fuel upon melting or as a result of further reaction of fuel and metal components with water inside the reactor vessel before release to the containment atmosphere.
2. Desorption from surfaces particularly from those of bare ferrous metals resulting in a

change in form from elemental or reactive iodine to methyl iodide occurring principally in the containment shell or building.

Gas phase reaction in the containment atmosphere is another potential source of methyl iodide but analytical studies conducted to date do not suggest that this is a significant source. The full interpretation of the direct release process must include the contribution from the recombination of highly ionized organic gases immediately adjacent to the fuel at the nearest region at a low enough temperature (300 to 400$^{o}$C) to permit recombination. Since there are many uncertainties involving favorable conditions (reducing) versus unfavorable (oxidizing) conditions in the gaseous effluent this process is difficult to assess.

Peters[21] has listed the following factors as probably contributing by the second process (desorption) to the formation of methyl iodide outside the reactor vessel: (It is comforting that there is no evidence which implicates painted surfaces as contributing significantly to methyl iodide production.)

1. Bare ferrous metal surfaces.
2. High surface-to-volume ratios exposed to the released iodine.
3. Reducing atmospheres.
4. Presence of organic gases.
5. Long aging periods.

6. Moderately high temperatures.
7. Moisture or steam.
8. High deposition velocities.
9. Low gas phase iodine concentrations.

## 4.3 Experience and Assessment of Methyl Iodide in Various Test Containment Facilities

A recent survey was made by Peters[21] in which the nuclear safety literature was sifted for the methyl iodide factor contributed by desorption process. The data were then correlated with both the concentration of iodine in the system, the residence time, and the size of the containment. The latter, he reduced to a simple surface-to-volume ratio. Table 2 below is a simplified interpretation of a comparison of the data compiled by Peters plus data on three ORNL installations, i.e., CMF, NSPP, HFIR.

Assuming that the observed percentage of methyl iodide was produced by desorption, it is interesting that a very good agreement for the methyl iodide conversion factor between the CMF and the NSPP is reached when a linear relation is assumed for both the surface-to-volume ratio and the residence time. For example, the data for the CMF[22] include all runs A, B, C, D, E, 3-25, 3-24, etc., except those in which organic gases were deliberately added. On this basis, 1% methyl iodide was generated in 5 hours from a vessel with a

Table 2. Methyl Iodide Observed in Various Containment Systems

| Facility | Material of Construction | Surface Volume$^{-1}$ Ratio, ft$^{-1}$ | Average Methyl Iodide Found (% of Inventory) | Hours in Containment |
|---|---|---|---|---|
| UKAEA (Windscale) | Carbon Steel 400°C | 1.5 | 5.0 | 20 |
| ADF (Hanford) | Painted Steel 20°C | 1.6 | 0.07 | 5 |
| Zenith | Painted Steel and Concrete, 25°C | 0.43 | 0.02 (ventilated) | 1 |
| Savannah River | Painted Steel and Concrete, 25°C | 0.09 | (0.002)* | 1 |
| CMF[22] | Bare Stainless Steel, 25°C | 2.8 | 1.0 | 5 |
| NSPP[23] | Bare Stainless Steel, 25°C | 0.43 | 0.5 | 30 |
| HFIR | Painted Steel and Concrete, 25°C | 0.12 | - | 0.45 (avg) |

*Predicted by Peters.

surface-to-volume ratio of 2.8. To calculate the expected equivalent in NSPP for 30 hours, it is only necessary to multiply the 1% observed in CMF by the time ratio 30/5 and the inverted surface-to-volume ratio $\frac{0.43}{2.8}$ which gives 0.9%. The estimate by Parsly [23] of the amount of methyl iodide in NSPP Run 7 after 50 hrs was 0.5%. Subsequent analyses of the data however indicates that the percentage is initially much higher and decreases during the time the fission products are aging in the containment vessel.

Similarly, the UKAEA test at Windscale gave 5.0% while the direct relation above predicts 2.0%. This probably reflects the effect of the higher temperature (400$^{o}$C); carbon steel, and/or the graphite paint used in the Windscale system.

The ADF and Zenith tests were both conducted in painted systems and these give much lower values than the metal systems by about a factor of 10.

It can then be seen readily that on this basis the expected HFIR condition indicates that only a negligible amount of methyl iodide will be formed by the desorption process.

## 4.4 Methyl Iodide Originating from the Fuel or in the Reactor Vessel

Since little direct evidence is available from which it is possible to estimate the amount of methyl

iodide originating from the fuel, a rather conservative point of view is necessary. In certain experiments at Windscale, Collins[16,24] has reported a number of results in all-glass equipment in which a special effort was made to preclude the origin of methyl iodide by the desorption process. These results are perhaps made more pessimistic by reason of the fact that the atmosphere was generally $CO_2$-CO mixtures. Seven experiments were described in which the methyl iodide observed ranged from 0.1 to 5.0 percent as measured by gas chromotography. The next highest result to the 5.0 percent was only 1.0 percent.

In another series of experiments reported by Collins[25] the percent of iodine release as organic iodides -- as indicated by selective adsorption on composite filter (May Pack) components ranged from 0.1 to 0.001 for fuel irradiations $\leq$ 7 MWD/t, and from 3 to 0.04 for fuel irradiations of 100 MWD/t.

Additional data on the fraction of released methyl iodide may also be obtained from analysis of the May Pack data from runs in the CMF[22] and the NSPP,[23,26] and range from 0.3 to 3.7 in the former and from <0.2 to 8.8% in the latter.

Some of the aforementioned data is presented in the following table together with relevant available information on the experiment from which it was obtained.

Table 3. Percent of Iodine Released as Organic Iodides in Various Experiments

| Experiment | Gas Composition | Fuel | % Iodine Release Fuel | % Iodine Organic Iodide | |
|---|---|---|---|---|---|
| | | | | Adsorbers | Gas Chromatograph |
| No. 21[16] | $CO_2$, 54%, CO 35% plus air, $H_2$, $H_2O$, etc. | $UO_2$, 150 MWD/T | 2.8 - 3 | 1 | 0.2 |
| No. 22[16] | $CO_2$/CO | $UO_2$, 150 MWD/T | 4 - 9 | 2 | 0.5 |
| No. 23[16] | $CO_2$/CO Sat. $H_2O$ | $UO_2$, 150 MWD/T | 40 | 4 | 5.0 |
| No. 24[16] | $CO_2$/CO plus $CH_4$ | $UO_2$, 150 MWD/T | 33 | 20 | 1.0 |
| No. 25[16] | $CO_2$/CO | $UO_2$, 150 MWD/T | 27 - 35 | 10 | Not done |
| No. 26[16] | $CO_2$/air | $UO_2$, 100 MWD/T | 25 - 47 | 2 | 0.7 |
| No. 27[16] | $CO_2$/5% $CH_4$ | $UO_2$, 150 MWD/T | 13 - 27 | 0.7 | 0.1 |
| Table 3[25] | Steam-air | $UO_2$, 0.5 MWD/T | 6.2 | 0.02 | |
| Table 3[25] | Steam-air | $UO_2$, 0.5 MWD/T | 6.8 | 0.02 | |
| Table 3[25] | Steam-air | $UO_2$, 1.0 MWD/T | 2.4 | 0.01 | |
| Table 3[25] | Steam-air | $UO_2$, 2.0 MWD/T | 2.4 | 0.02 | |
| Table 3[25] | Steam-air | $UO_2$, 5.0 MWD/T | 2.9 | 0.001 | |
| Table 3[25] | Steam-air | $UO_2$, 1.0 MWD/T | 13.7 | 0.1 | |
| Table 3[25] | Steam-air | $UO_2$, 2.0 MWD/T | 15.4 | 0.003 | |
| Table 3[25] | Steam-air | $UO_2$, 7.0 MWD/T | 40.5 | 0.03 | |
| Table 4[25] | Steam | $UO_2$, 100 MWD/T | 28 | 0.04 | |
| Table 4[25] | Steam | $UO_2$, 100 MWD/T | 35 | 0.5 | |
| Table 4[25] | Steam | $UO_2$, 100 MWD/T | 34 | 3 | |
| Table 4[25] | Steam | $UO_2$, 100 MWD/T | 9 | 2 | |
| Table 4[25] | Steam | $UO_2$, 100 MWD/T | 27 | 0.08 | |
| Table 4[25] | Steam-air | $UO_2$, 100 MWD/T | 60 | 0.2 | |
| A[22] | Air | $UO_2$ trace | 83.8 | 3.7 | |
| B[22] | Air | $UO_2$ trace | 63.8 | 0.4 | |
| C[22] | Air | $UO_2$, 7000 MWD/T | 90.9 | 0.3 | |
| D[22] | Air | Iodine only | 91.6 | 0.5 | |
| E[22] | Air | Iodine only | 100 | 0.3 | |
| Run No. 6[26] | Air | Iodine only | ~ 100 | 8.8 | |
| Run No. 7[23] | Air | $UO_2$ and Iodine | ~ 100 | 8.4 | |
| 27 | He | $UO_2$, 2000 MWD/T | 30 | 5 | |

Considerable caution needs to be exercised in the interpretation of the above information because of the wide variety of experimental conditions which are represented. It is unfortunate that most of the data must be inferred from May Pack data which is known to give higher results for the methyl iodide fraction than can be confirmed by more sensitive gas chromatographic techniques. Furthermore, much of the data has been obtained in experiments employing CO and/or $CO_2$. Another important factor is the amount of iodine involved in the release, inasmuch as the iodine concentration appears to be significant in determining the percentage of methyl iodide formed.[27] The seeming dependence on fuel exposure as suggested in reference 25 is not borne out in other experiments in which fuel with much higher burnups have been employed.

Assessing the above data as applied to the HFIR MCA release is therefore a difficult and somewhat nebulous business. It is our considered opinion, however, that of the iodine considered to be released from the fuel in the HFIR, MCA less than 5% of the iodine inventory will exist in the containment vessel in the form of methyl iodide. It is noted that this estimate is comparable but somewhat higher than similar estimates made by workers in this field outside ORNL.[(a)]

(a) A. H. Peter of Savannah River suggested 1% in September 1965, D.A. Collins of UKAEA suggested 2% in April 1965.

# 5. ADSORPTION OF METHYL IODIDE BY ACTIVATED CHARCOAL

## 5.1 Introduction

The following is an attempt to marshal information available at the present time to formulate an estimate of the iodine trapping efficiency which can be expected of the SBHE gas cleaning system. In the last few years it has become apparent that iodine can and does exist in at least two forms or groups of forms which are of direct interest to nuclear safety activities, i.e., elemental iodine and organic iodides, of which methyl iodide is the most difficult to trap. These two forms are quite different in nature and consequently behave differently in gas cleaning systems.[28-32] Consequently, in evaluating the expected effectiveness of the SBHE gas cleaning system, it is necessary to consider both forms.

Elemental iodine vapor is quite readily adsorbed from a gas stream onto the surfaces of activated charcoal and once on the surface it is immobilized and consequently is difficult to remove by continued gas flow. The forces which hold the iodine molecule to the charcoal surface are very similar to those present in chemical compounds. This adsorption process, in the case of elemental iodine vapor, is rather insensitive, within limits, to temperature, iodine concentrations in the gas, humidity of the gas, duration of gas flow,

gas velocity through the charcoal mass, contaminants on the charcoal surface, and depth of charcoal mass. Elemental iodine vapor is therefore rather easily removed by activated charcoal from gas systems.[28,29,31,32] The existing SBHE charcoal filters (properly installed) would be expected to remove elemental iodine vapor with an efficiency greater than 99.9% under stated accident conditions of 70% relative humidity and gas velocity of 50 ft/min.

The removal of methyl iodide vapor from gas systems presents a more difficult problem. It appears that the bonding of methyl iodide molecules to the charcoal surfaces is physical rather than chemical in nature. These bonding forces are affected to a large degree (as compared to those between $I_2$ and charcoal) by system conditions such as temperature, humidity, gas velocity, duration of gas purge, and depth of charcoal. Work is in progress to study the inter-relationships of these variables.[28,33]

## 5.2 Factors Affecting the Trapping of Methyl Iodide

While all of the system variables, listed above, are important, probably the most important is the humidity of the gas stream, or specifically, the resulting moisture content of the charcoal when exposed to gas flow of this humidity. The adsorption of water by charcoal is rather different compared to the

adsorption of other vapors[34,35] and this difference must be appreciated in order to explain the observed detrimental effects of adsorbed water vapor on the adsorption of methyl iodide molecules. Figure 1 shows the moisture adsorption behavior of the Barnebey-Cheney charcoal contained in the SBHE charcoal filters.[36] At low relative humidities (up to about 10 to 20%) only a small amount of water per gram of charcoal is adsorbed. Under these conditions, the interference with methyl iodide adsorption is significant, though small. Over the humidity range 20 to 80%, the quantity of water adsorbed per gram of charcoal increases rapidly. This is due to capillary condensation within the pores of the charcoal granules. In effect, many of the pores are blocked by liquid water and the entrance of methyl iodide is prevented. The interference with methyl iodide adsorption can be quite large. In the higher humidity range, > 80%, some additional water is taken up because of additional condensation of water in the larger pores. Under this condition the retention of methyl iodide by charcoal is very inefficient. The foregoing illustrates generally the magnitude of the effect of adsorbed water on the adsorption of methyl iodide and the need to control the humidity of the off-gas stream, if possible.

The other system variables influence the adsorption of methyl iodide in much the same manner as the

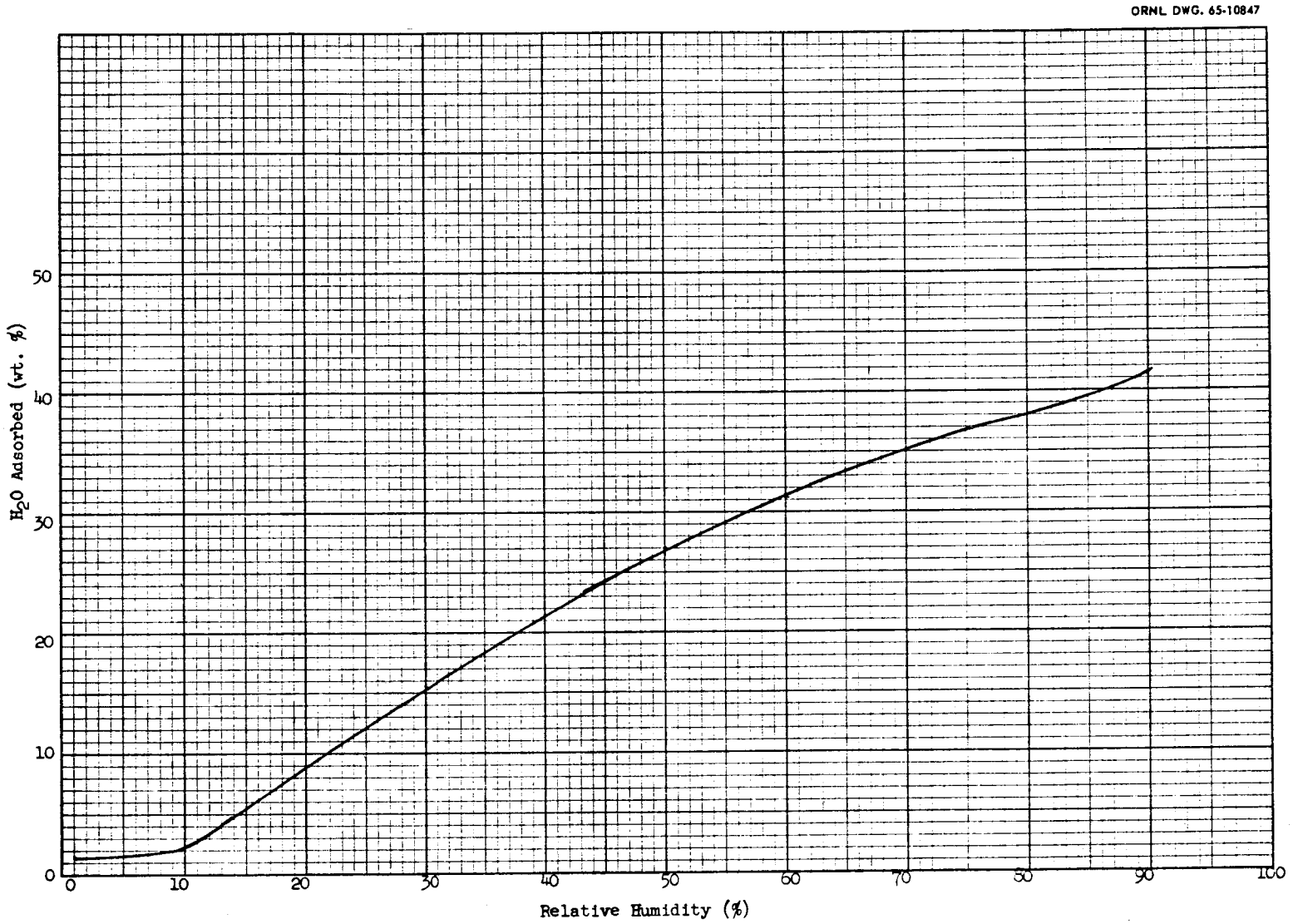


Fig. 1. Adsorption of $H_2O$ Vapor by Barnebey-Cheney Activated Charcoal

adsorption of any gas on charcoal. In general, methyl iodide will be retained more efficiently by charcoal, the lower the temperature, the lower the gas velocity, the shorter the duration of gas purge, and the greater the depth of charcoal.

## 5.3 Methyl Iodide Data Most Directly Applicable to HFIR-SBHE System

It is assumed that the following conditions will be present, or methods of operation will occur, following a partial meltdown of a core at the HFIR. The charcoal beds in the SBHE system will have been exposed for a long period of time to air flow at an estimated relative humidity of 60 to 70%, and will contain an equilibrium quantity of water vapor for this condition. Approximately 5 grams of fission product iodine will be released into the reactor bay and will be subsequently removed by the SBHE system over a period of two hours. Gas flow through the charcoal filters will continue for an unspecified time. It is possible that a significant quantity of the released iodine may exist as or be converted to methyl iodide before reaching the charcoal filters. An estimation of the performance of the existing SBHE off-gas system under these conditions follows.

Laboratory data, under conditions approaching these, have been obtained by two groups within the

Nuclear Safety Program. The results by both groups are in substantial agreement as to the behavior of methyl iodide in Barnebey-Cheney charcoal Type 513, the type used in the SBHE filter. This experience indicates that elution of methyl iodide from the HFIR type of charcoal occurs upon continued gas flow.

On the basis of this data, the following estimation of performance can be made. After two hours of operation of the SBHE system following an accident the efficiency for methyl iodide will probably be about 85% if air flow is stopped at this time. Upon continued air flow, additional elution of methyl iodide will occur. For example, at 5 hours the efficiency will have dropped to approximately 57%, at 15 hours to about 46%, and at 25 hours to about 43%.

## 5.4 Possible Modification of SBHE System

It has been suggested that the SBHE system or its operation might be modified in some way so as to obtain a higher efficiency for methyl iodide. These modifications might include substituting a different adsorbent material, reducing the air flow (or possibly stopping air flow after some interval of time), increasing the depth of charcoal, or dehumidifying the air stream.

Substitution of a different adsorbent material is a very promising modification. A form of coconut charcoal, specially treated by Mine Safety Appliance Company,

has been highly effective in trapping radioactive methyl iodide under HFIR accident conditions.[37] Non-radioactive methyl iodide is observed emerging from the adsorber while it is trapping radioactive methyl iodide, suggesting that an exchange process is at work. That iodine exchange is the explanation is borne out by the finding that the specially treated charcoal contains iodine. Further work on this adsorbent is underway to determine the optimum conditions for its application and to identify adverse conditions which must be avoided. Quite possibly products of other manufacturers will be equally effective. Based on data now available it should be possible to obtain 92% efficiency for trapping methyl iodide in a 1 in. bed of the special MSA charcoal after 28 hours of air flow under HFIR conditions. Under the same conditions a 2 in. bed of the special MSA charcoal would yield a 99.7% efficiency. Additional data are presented in Fig. 2.

Some improvement in methyl iodide efficiency can be obtained in the present SBHE system without changing the identity of the charcoal. By decreasing the flow rate in the system, the linear velocity of air through the charcoal mass will be reduced and consequently the time required for penetration of methyl iodide will be increased. Direct data under SBHE conditions are not available; therefore, data acquired under conditions

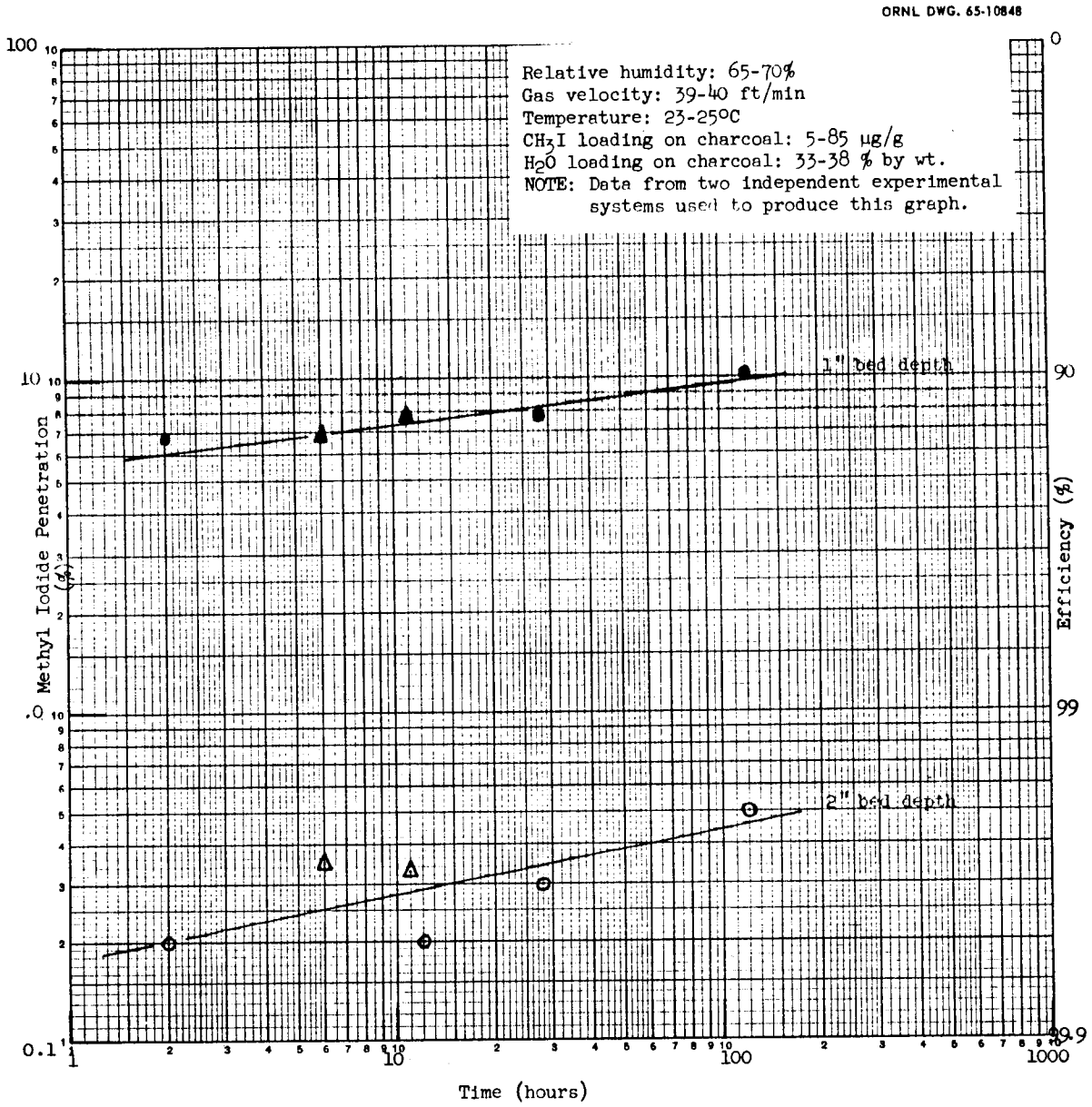


Fig. 2. Efficiency of MSA Charcoal Under HFIR Accident Conditions

simulating those expected in large power reactors where the concentrations of iodides in the off-gas system would be expected to be large, will be used.[28] Experimentally, methyl iodide was loaded onto ordinary charcoal continuously over the duration of the experiment and samples of the gas processed by gas chromatography. These conditions were chosen in order to determine the charcoal efficiency under the relatively unfavorable conditions when loadings of methyl iodide are as high as 4.4 mg of methyl iodide per gram of charcoal. While these loading conditions are much higher than those expected in the SBHE, data gained in this series of experiments permits an estimation of benefits that might be gained by reducing the volume flow rate of the SBHE system. As an example, after 2 hours of operation at 50 ft/min linear velocity and 60% relative humidity, a 1 in. bed of PCB charcoal had an indicated efficiency of 88.9%; under the same conditions, except a linerar velocity of 10 ft/min, the efficiency was 99.9%. After 5 hours the efficiencies were 75 and 94%, respectively.

If the air flow could be stopped at some interval of operation after the accident, say 2 or 3 hours, then many of the problems could be circumvented by using the off-gas system as a container for the contaminated gases. However, this method of operation probably should be considered only as a last resort.

Increasing the charcoal depth to 2 inches would be of some benefit in increasing the time required for breakthrough of methyl iodide, but upon continued air flow the efficiency is limited for ordinary charcoal because of leakage of methyl iodide from the charcoal. After two hours of operation, a 2-inch bed of charcoal has an efficiency for methyl iodide of > 99.9%, as contrasted to 85% for a 1-inch depth of charcoal. However, after approximately 25 hours of operation the efficiency of the 1-inch charcoal system dropped to 43% while that of the 2-inch system dropped to 57%.

Dehumidification of the air exhaust into SBHE from the HFIR building would produce the largest increase in the efficiency of ordinary charcoal for methyl iodide. To illustrate the effect of adsorbed water, an experiment with SBHE charcoal was performed in which all the SBHE accident conditions were used, except the relative humidity of the air sweep was reduced from 65 to 35%. Retention of methyl iodide was more efficient for a longer period of time. For a 1-inch depth of ordinary charcoal the efficiencies at 2, 5, and 15 hours were 99.6, 95.6, and 79.5%, respectively. For a 2-inch depth of charcoal the efficiencies at 2, 5, and 15 hours were 99.9, 99.8, and 98.7%, respectively. These data are compared with those from the 65% relative humidity experiment in Table 1.

Of the various modifications considered, use of a specially treated charcoal seems most promising. The effects of conditions on the efficiency of this new material are being investigated. The other possible modifications could yield additional benefit.

## 5.5 HFIR Charcoal Efficiency for Methyl Iodide

In summary, the charcoal adsorbers now installed in the SBHE system of the HFIR will produce an efficiency of approximately 85% for methyl iodide over a two-hour period of operation at a linear velocity of ~ 40 ft/min under a humidity of 60 to 70%. The efficiency under continued operation will be reduced as methyl iodide is eluted from the charcoal. For example, after approximately 5 and 15 hours of operation, efficiencies will be approximately 57 and 46%, respectively. Reducing the gas flow rate, increasing the depth of charcoal, or lowering the humidity of the gas stream will increase the efficiency of charcoal for methyl iodide retention in a gas system. Substituting a specially treated charcoal will yield substantial benefit.

Table 4. Methyl Iodide Tests Under SBHE Conditions

| Elapsed time (hr) | Efficiency at Charcoal Depth of | | | | | |
|---|---|---|---|---|---|---|
| | 0.5 in. | | 1.0 in. | | 2.0 in. | |
| | 60-70%* | 35% | 60-70% | 35% | 60-70% | 35% |
| 2 | 59.9 | 92.1 | 85.2 | 99.6 | >99.99** | 99.9 |
| 5 | 36.8 | 73.6 | 56.8 | 95.6 | 90.7 | 99.8 |
| 15 | 33.7 | 54.2 | 46.1 | 75.6 | 65.1 | 96.3 |
| 25 | 33.7 | - | 43.1 | - | 56.9 | - |

*Relative humidity of air

**Efficiency dropped to 99.6 at 2.5 hours.

Test Conditions: Relative humidity as indicated above; gas velocity, 38-40 ft/min; temperature, 23-24°C; methyl iodide loading on ordinary charcoal, 5-10 μg/g.

# 6. DISCUSSION AND RECOMMENDATIONS

This study of the HFIR filter system, the evaluation of its performance, and the following recommendations were all made from the point of view that the system constituted an engineered safeguard which was of necessity incorporated into the analysis of the MCA in order to reduce the resultant exposures therefrom. Thus, in situations where the experimental data are incomplete, only the most conservative interpretation and/or extrapolation have been employed rather than to use what otherwise might be considered the most probable information. This approach was followed in order to provide a basis for determining the performance of the system which we believe will not only be adequate to cope with the consequences of the MCA but also be acceptable to the ACRS and the Commission's regulatory staff.

The concern which lead to the compilation and examination of the preceding data arose from the knowledge that in some fuel element melt experiments significant quantities of methyl iodide were formed and that in some filter tests under humid conditions the filter efficiencies were much lower for methyl iodide than for molecular iodine and decreased with continued operation. Therefore, to ascertain the performance of the HFIR containment system all known relevant data on methyl iodide release and behavior were examined. Furthermore, some additional experimental work was performed in an attempt to resolve or understand

discrepancies between apparently conflicting data on the removal of methyl iodide by charcoal.

The problem quickly resolved itself into two main areas: (1) of the iodine released in a fuel melt what fraction could appear as methyl iodide, and (2) what is the filter efficiency of charcoal for methyl iodide under the worst accident conditions. A corollary question was: should the resulting iodine release be unacceptable from a safety standpoint, what changes should be made in the HFIR filter system so that the release would be acceptable?

Experience on the fractional release of iodine as methyl iodide was considered first. Although information on the formation of methyl iodide has been accumulated particularly in the US Nuclear Safety Program and that in the UK, the data are not without its ambiguities, difference in experimental facilities, and procedures, as well as inadequacies in characterization and analytical techniques. Evaluation of all the existing information on the quantity of methyl iodide formed as a consequence of the initial fuel element melt has led us to the conclusion that in all probability the amount is less than 5% of the iodine inventory. Since methyl iodide is known to be formed as a consequence of both the reaction of molecular iodine with organics in the air and the reaction of molecular iodine with impurities on the exposed surfaces, as well as during the release process, the percentage of methyl iodide is expected to be a function of the residence time in the

container as well as the surface-to-volume ratio of the contained volume. Simple analytical models which have been developed to extrapolate from one geometry to another imply if methyl iodide fraction found in the static conditions existing in the CMF or NSPP were due to surface reactions, it would correspond to a percentage of methyl iodide two orders of magnitude less in a large ventilated containment system. However valid this argument may be on theoretical grounds, this factor of $\sim 10^{-2}$ was not considered further in this analysis, and the 5% value recommended above was taken as an upper limit from numerous experiments in which it was attributed primarily to the release process.

It was concluded in Section 3 that an iodine decontamination factor of 20 would limit the maximum total integrated thyroid dose to ~ 300 rem. From the data presented herein it may be assumed that after one day (actually 25 hrs) the efficiency of the present HFIR charcoal trap for methyl iodide was 43% and the $CH_3I$ accounted for 5% of the iodine, whereas the removal efficiency for the remainder of the iodine presumed to be molecular or on particulates was >2000. Thus, the overall removal factor for iodine would actually be greater than 20 at that time. It is noted that the calculation assumes that the air flow stops at 25 hrs.

Should the project wish to improve the methyl iodide removal efficiency of the system it could do one or more of the following:

1. substitute a specially treated charcoal
2. increase charcoal depth
3. decrease flow rate
4. decrease moisture content of the ambient aerosol
5. reduce flow time

Some data on the increased efficiency which might accrue from each of these changes was presented in Section 5, and testing of various charcoals under the indicated conditions is continuing.

In view of the performances of MSA impregnated charcoal for the removal of methyl iodide from moist atmospheres, it is recommended that this type charcoal be employed in the HFIR-SBHE system rather than the Barnebey-Cheney Type 513 charcoal now specified. The recommended charcoal is described in more detail in Appendix A. Furthermore it would appear that the HFIR charcoal absorbers could be conveniently increased in thickness to two inches with no loss in system performance and the change should be made for the improved efficiency which would result. Other methods (3-5 above) of improving iodine removal efficiencies are also available but do not appear to be warrented or necessary in the HFIR system.

It is further noted that any engineered safeguard such as the filters in the SBHE system should be periodically tested under simulated accident conditions. In view of the present state of knowledge of $I_2$ and $CH_3I$ adsorption on

charcoal, it is recommended that the basic filter test consist of in-place tests with DOP, $I_2$ and radioactive $CH_3I$. Techniques for in-place testing with methyl iodide are being developed.

The reliability and operability of the remainder of the filter system must be similarly demonstrated and periodically tested including blowers, power supplies, and switching valves.

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Appendix A: Specification of Charcoal Recommended for Use in HFIR SBHE Filters

# INTRA-LABORATORY CORRESPONDENCE

**OAK RIDGE NATIONAL LABORATORY**

**September 22, 1965**

**To:** Frank T. Binford
Bldg. 3001

**cc:** W. E. Browning, Jr.
T. E. Cole
F. L. Culler
J. W. Hill, Jr.
G. W. Parker
G. M. Watson

Subject: Charcoal for HFIR Filters

The identification of the charcoal which we recommended for use in the HFIR adsorber as contained in my letter of September 20 is misleading. We have obtained further information from MSA to the effect that they subject the as-received Barnebey-Cheney charcoal to two propriety treatments; i.e., first, they increase the surface area - second, they impregnate it. After the first step the charcoal is designated MSA 25725, and after the second it is designated MSA 85851. We recommend that the MSA 85851 charcoal be used in HFIR. This is the same charcoal which is used in the MSA-CU-85241 chemical filters.

Original signed by

**Wm. B. Cottrell**

**WBC:mmb**

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