SEMINAR ON

# Iodine

# Filter

# Testing

Volume II

Karlsruhe (W. Germany), 4–6 December 1973

*PROCEEDINGS – ACTES – TAGUNGSBERICHTE*

# Seminar on
# IODINE FILTER TESTING

# Séminaire sur
# L'ESSAI DES FILTRES A IODE

# Seminar über
# JODFILTER UND IHRE PRÜFUNG

*Seminar organized by the*
*Directorate-General Social Affairs*
*Directorate Health Protection*
*Karlsruhe (W. Germany), 4-6 December 1973*

Volume II

# C O N T E N T S

## PRELIMINARY REMARKS

As announced in Volume I of the "Proceedings of the Seminar on
Iodine Filter Testing", a summary of the discussions which took place
during the technical sessions is published in this booklet. The Chair-
men of sessions I-IV have been kind enough to provide a critical ana-
lysis of and commentary on those discussions, for which we should like
to express our sincere thanks.

The chapters "Basic Elements" and "Test Methods and Operational
Experience" have also been published in the original French and German
versions. In answer to many requests, an English translation of a
basic seminar paper on "Behaviour of Iodine Sorption Materials" is
also included.

In this way, it is hoped to reach as wide an audience of spe-
cialists as possible and to give - in addition to the comprehensive
account of the state of the art as presented in Volume I of the
Seminar Proceedings - a critical analysis of the problems still out-
standing in iodine filter techniques and to indicate especially those
problems whose solution should be given priority in the near future.

The Secretariat


## REMARQUE PRELIMINAIRE

Comme l'annonçait le volume I des actes du séminaire sur l'essai
des filtres à iode, le présent fascicule, qui constitue le volume II,
donne un résumé des discussions d'ordre technique intervenues lors de
ce séminaire. Les présidents des séances consacrées aux aspects tech-
niques se sont efforcés d'analyser et de commenter ces discussions;
qu'ils en soient, ici, une fois encore, remerciés.

Les contributions "Basic Elements" et "Test Methods and Opera-
tional Experience" sont publiées en anglais ainsi qu'en version ori-
ginale, allemande ou française. Pour répondre à la demande générale, ce
volume donne aussi une traduction vers l'anglais de l'exposé de fond

sur le "comportement des matériaux utilisés pour la sorption de
l'iode", fait lors du séminaire.

On espère ainsi que ce volume, venant s'ajouter à la présentation
complète de l'état de la technique qui figure au volume I, recevra la
plus large audience dans les milieux intéressés, à qui il fournira
une analyse critique des problèmes encore latents relatifs à la fil-
tration de l'iode ainsi qu'un ordre des priorités à cet égard.

<div align="right">Le Secrétariat</div>

## VORBEMERKUNG

Mit diesem Bändchen wird - wie im Band I der Proceedings on
the Seminar on Iodine Filter Testing angekündigt - eine Zusammen-
fassung der Diskussionen in den Sitzungen, die bei diesem Seminar
technischen Aspekten gewidmet waren, veröffentlicht. Die Chairmen
der Sitzungen I-IV haben sich der Mühe unterzogen, diese Diskussionen
kritisch zu analysieren und zu kommentieren, wofür ihnen auch hier
herzlich gedankt sei.

Die Beiträge "Basic Elements" und "Test Methods and Operational
Experience" werden zusätzlich auch in der Originalfassung französisch
bzw. deutsch abgedruckt. Auf vielfachen Wunsch wird ausserdem ein
Grundlagen-Vortrag des Seminars über das "Verhalten von Jod-Sorptions-
materialien" in englischer Uebersetzung wiedergegeben.

Es wird erhofft, auf diese Weise einen möglichst weiten Inter-
essentenkreis anzusprechen und diesem ausser einer abgerundeten Dar-
stellung des Standes der Technik, wie sie der Band I der Proceedings
bringt, auch die offenen Probleme der Jodfilter-Technik zu vermitteln
und Prioritäten für deren Lösung aufzuzeigen.

<div align="right">Das Sekretariat</div>

BASIC ELEMENTS *)

Paul Sigli

INTRODUCTION

The first session of this Seminar was devoted to the basic principles governing iodine trapping. The problem posed by the fission product, iodine-131, is a critical factor particularly in the event of reactor accidents; for more than ten years now research workers in all countries using nuclear energy have been trying to limit its release. For this reason studies on the physical or chemical behaviour of elemental iodine or its compounds have resulted in the design of filters and traps aimed at controlling any discharge into the environment. Materials capable of retaining gas-borne iodine in all its forms, under varying operational conditions, have therefore been developed for this purpose.

The six papers of this first session accordingly dealt with :

- the general properties of sorbents in relation to different compounds of iodine;

- different forms of iodine which might appear in the course of an accident, and the origin of these forms;

- the ageing of these sorbents, an important problem, since it is a major factor in determining the policy to be followed to ensure a really efficient iodine retention in the event of gaseous discharges to the atmosphere.

In this account, which summarizes the work of the first session, each of the above points will be dealt with. Since the main ideas have been expounded by the various authors, an attempt has been made to extract from the discussion the essential points raised by the participants, clarifying them if necessary, to try and pinpoint the research which still seems necessary. However, as far as the general properties of sorbents are concerned,

*) Bibliography see p. 73; French version see p. 45

the account is confined to a short summary; fuller details can be found in the opening paper of the Seminar /1/.


# 1. IODINE TRAPPING CONDITIONS

The first stage in planning devices for trapping vapour forms of iodine is to select a suitable sorbent; this will include the study of its behaviour as a function of the different physico-chemical forms envisaged.


## 1.1. Sorbent materials

The sorbent most frequently studied in recent years is undoubtedly charcoal*). It generally displays good retention qualities in relation to molecular iodine, but it can be penetrated by methyl iodide, particularly if the relative humidity is high. This is illustrated in Figure 1, Volume I, page 5 of the paper presented by J.G. WILHELM **). This disadvantage of activated charcoal has been overcome by impregnating it either with triethy-lenediamine (TEDA) generally in the proportion of 5 %, or with potassium iodide or even with elemental iodine (or a mixture of the two latter mate-rials) in proportions varying from 0.5 to a few percent.

The grain size of the charcoal used has a very strong influence on the final result. If the grain size is reduced, the efficiency increases. However, the pressure drop, which also increases with reduction in grain size, will then be a limiting factor. For practical purposes, the useful grain size that can be adopted corresponds to diameters normally between 1 and 4 mm, but in the case of extruded material the length may be greater.

These sorbents, however, have the disadvantage of being affected by nitrogen oxides ($NO_2$ in particular) and of being able to operate only at

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*) Charcoal in the context of this report means activated charcoal or activated carbon.

**) English version see this volume p. 77

relatively low temperatures. As a consequence, silver-impregnated materials were developed, based on molecular sieves, or the product AC 6120 *) /1/, the properties of which made them suitable for work in conditions under which charcoals could no longer be used. This is particularly true of the use of a solid sorbent for fuel reprocessing plants, in which the use of charcoals is ruled out because of the nitrogen oxides and the risks of fire or even explosion.

## 1.2. Influence of carrier gas humidity on efficiency

The sorption of elemental iodine and methyl iodide is reduced if the active surface of the sorbent has taken up water. This phenomenon is particularly noticeable in the case of methyl iodide. At relative humidities below 30-40 % there is little effect on retention efficiency, but as humidity rises retention efficiency falls, principally above the 70 % level. Materials have been developed which will deal with relative humidities up to near 100 %.

## 1.3. Sorption at high temperature

Raising the temperature – sometimes made necessary if the relative humidity is high – can affect the impregnated charcoal in the following ways /1/ :

- Loss of impregnant with consequent deterioration of the properties of the sorption bed;
- Desorption of the products which had been retained initially;
- Ignition of the sorption bed.

The practical upper limit for the use of an impregnated charcoal in air will generally not be below 100°C. Above this temperature the limit should be established for each material. If operation at even higher temperatures cannot be avoided inorganic sorbents mentioned above would have

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*) Specially prepared amorphous silicic acid impregnated with silver nitrate.

to be used.

## 1.4. Influence of iodine concentration in the carrier gas

Iodine concentrations in the ventilation air flow of a reactor under normal operating conditions reach very low values, for example $10^{-4}$ to $10^{-6}$ $\mu g \cdot m^{-3}$. The problem then is to find out how the efficiency of the sorbents is affected when the iodine concentration in the carrier gas reaches such low levels.

A reduction in efficiency at low iodine concentration has been reported both for charcoals and silver-impregnated zeolites /2/. However, WILHELM /1/ states that it is not possible to set a concentration value at which such a reduction occurs.

The German work shows, moreover, that there is a difference in filter performance depending on whether the concentration of $CH_3I$ is produced by dilution in the air or by preceding filtration. In the former case the performance for low and high concentrations is identical over a range representing a factor of $10^9$, whereas in the latter case, efficiency drops after prefiltration at low and at high concentrations. This suggests that perhaps not only the effect of concentration is under study but also the effect of a new species more penetrating than the test agent. This question will be examined again in greater detail in Section 2.1.

## 2. THE PHYSICO-CHEMICAL SPECIES OF IODINE PRESENT IN A REACTOR

## 2.1. Demonstration of the presence of methyl iodide and penetrating species

As a result of experiments carried out in Britain, MEGAW and MAY /3/ showed that the elemental iodine introduced into the containment of the reactor Pluto disappeared quickly, whereas a residual fraction seemed much more difficult to trap. EGGLETON and ATKINS /4/ /5/ then applied themselves to identify this fraction which had proved difficult to sorb.

The iodine was generated from sodium iodide, passed over a copper knit-
mesh and filtered, the part thought to be penetrating then being condensed
in a cold trap. Whereas one fraction of this, which was soluble in benzene
and water, remained unidentified, the second fraction was identified as an
alkyl iodide, the two main constituents being methyl iodide (85 %) and ethyl
iodide (3 %). These studies, which revealed for the first time the penetra-
ting species of iodine, were of the utmost importance, since they were to
establish the pattern of research for the next ten years. Methyl iodide does
in fact behave like a penetrating species.

As work proceeded on the behaviour of filters for trapping methyl
iodide, it became apparent that at least one species was proving to be even
more penetrating than methyl iodide (see for example /1/ page 12, figure 5).
At the 10th Air Cleaning Conference, F.O. CARTAN, H.R. BEARD, F.A. DUCE
and J.H. KELLER /6/ emphasized that a non-organic penetrating species was
trapped on oxide of hydrated zirconium loaded with iodine. This species,
according to the authors, might be hypoiodous acid HIO. The main objection
raised to this hypothesis was that hypoiodous acid was not only unstable,
but also largely non-volatile. The 11th Air Cleaning Conference yielded
from the same authors /2/ an attempt to identify the compound involved.
Nevertheless, it remains true that the hypothesis of the existence of
hypoiodous acid as a penetrating species can be justified only by indirect
evidence and that further confirmation is clearly required.

At the Karlsruhe Seminar, WILHELM put forward the idea that iodic
acid $HIO_3$ might also have sufficient vapour pressure for it to be found
in the gaseous phase, and thus lead to an inorganic form which would be
difficult to trap. However, the German studies do not, at the present stage,
permit a definite conclusion to be drawn.

During discussion it was commented that research elsewhere on the
trapping of small concentrations of methyl iodide indicates that the higher
penetrations observed under these conditions are not necessarily due to
the effect of concentration alone but might well result from a highly pene-
trating species. The existence of this species could only be confirmed when
the efficiency of the sorbents used had reduced the methyl iodide activity
by several orders of magnitude so that the activity of an "impurity" became
dominant. In fact the whole difficulty of such a study, involving very

small concentrations of iodine, becomes clear if we remember that the
air we breathe contains per cubic meter a quantity of methane of the order
of $\mu$g, and a quantity of iodine of the order of $10^{-3}$ $\mu$g. Because of
the high reactivity of iodine, in the course of generating methyl iodide,
we could very well produce an impurity, whether representative or not of an
actual case in a reactor, which might at times considerably distort the
results of a laboratory experiment.


## 2.2. The physical forms of iodine

Throughout what has been said before we have implied to some extent
that we are interested in the strictly gaseous phase. The paper by PFEIFFER
/7/ shows that we must also take account of aerosols and the author gives
the composition of the activity that he has been able to detect in the BWR
reactor at Gundremmingen. By means of a sampler consisting of :
- asbestos fibre filters,
- activated charcoal cartridge,
- cartridge with activated charcoal impregnated with 1 % potassium
  iodide,
- and filter elements of AC 6120 impregnated with silver,
which he combined in various sequences, the author arrived at the conclusion
that the distribution of activity takes place in the following way (at the
ventilation stage) :

- aerosols : 40 %
- substances easily trapped by activated charcoal : 50 %
- penetrating species : 7 %

PFEIFFER also notes that this composition varies greatly as a function
of sampling point.

Several explanations are possible for this significant quantity of
iodine in aerosol form. It may be a case of liquid or solid aerosols in
which iodine is either an integral part of the aerosol or merely attached
to it by sorption. Whatever the case may be, the author notes that these
aerosols are only partially trapped on the activated charcoal. Two experi-
ments conducted in conjunction show that the filter of the first pack
placed downstream from the charcoal filter elements produces an activity

similar to that extracted by the filter of the first pack, placed upstream.
This experiment furthermore proves that aerosols are not formed on the
charcoal (sorption on the dust of the activated charcoal, for example).

## 2.3. Origin of the iodine

In BARBIER's paper /8/ the suggestion is put forward that the
iodine-131 discharged from a reactor into the atmosphere could be derived
from the precursor tellurium-131, which is not trapped either by the
high-performance filters or by the activated charcoal filter.

Experiments carried out in Britain /9/, however, have shown that
samples of irradiated fuel, heated in carbon dioxide so that the stainless
steel cladding and part of the fuel itself melted, would allow the escape
of the fission products Te-132, Cs-137 or Sr-90 in the form of particles
which could then easily be trapped on the filters (HEPA type).

Moreover, in discussion it was pointed out that there may be insuffi-
cient tellurium volatilised to explain the high release of iodine. This
gives support to the idea that the amount of iodine in the coolant gas or
liquid is not determined to any great extent by its parent nuclide.

The importance of the presence of tellurium in the cooling circuit
does not yet seem to be clearly determined, but a series of experiments
could be designed to throw some light on this particular point.

## 2.4. Origin of methyl iodide

Two papers /10/ /12/ referred to the behaviour of iodine in a reactor.
The first paper of HILLARY /10/ reported the behaviour of fission product
iodine-131 emanating from defective fuel elements which was released into
the coolant and, in addition, the behaviour of methyl iodide which was
intentionally introduced into the reactor. In the former case, the iodine
was found to occur mainly in the form of methyl iodide, while up to at most
10 % occurred as aerosol or elemental iodine. However, the author notes that
it is highly probable that some of the particulate iodine or the molecular
iodine may have settled on the sampler piping with possible distortion of

the final result. Lastly, the ratio of the quantity of iodine released from the fuel to that found in the gas was (after decomposition/deposition) 4 500 which represents the decontamination factor of the entire installation. The methyl iodide which was intentionally introduced into the reactor cooling circuit displays behaviour similar to that of the fission iodine (in that its rate of removal was rapid, at least initially).

The experiment carried out in France /12/ on the Chinon-I-gas-graphite reactor consisted of injecting elemental iodine into the coolant circuit. The principal conclusions were :

- iodine is found from the time of the first measurements in penetrating form;
- the concentration of this penetrating form decreases rapidly with time.

It may be noted that these two papers in point of fact reach a similar conclusion : the preponderance of penetrating species in the gaseous phase and the trapping of these species by the reactor structures.

Finally, it is precisely the composition of the gaseous phase, and the species encountered in it, which interest the scientist whose task it is to foresee what may happen in the event of an accident, in order to determine its behaviour in discharges to the atmosphere. In fact, it may be that methyl iodide does not originate in the fuel itself, any more than in the liquid phase (in the case of LWRs) but in the gaseous phase. A critical study by POSTMA and ZAVADOSKI /13/ on the possible origins of methyl iodide concludes that the most likely origin is a process of radiolysis, in the gaseous phase. As stated above, the air contains organic impurities in quite substantial quantities. The air in an LWR containment building will be even more loaded with organic vapours from a wide range of sources, and, in the event of an accident, it will be under prolonged exposure to high levels of radiation, thus creating a proportion of free radicals, principally $CH_3$, naturally resulting in the formation of methyl iodide. Finally, the American authors conclude for a specific case and prescribed time interval that methyl iodide must represent something like 3 % of the iodine present in the gaseous phase, this iodine itself representing only 25 % of the total core inventory.

It must be appreciated that these figures, which are much lower than those above put forward, are not necessarily incompatible. The high percentages of methyl iodide, arising in normal operation of gas-cooled reactors might then be interpreted as the result of an apparent enrichment arising from the disappearance of the elemental form by attachment to reactor surfaces. A similar phenomenon would occur with any reactor : the proportion of methyl iodide should increase in proportion to the distance from the point at which the iodine was released.

Another point of interest concerns the species of iodine present at the point of discharge. There is no doubt that, if the relative proportion of methyl iodide increases, the risk of contamination of the grass-cattle-milk-food chain is likewise minimized.

Knowledge of the origin of the formation of methyl iodide and its probable proportion in discharges to the atmosphere leads to a more precise approach to the risk arising from an accidental discharge of iodine. Although numerous studies have already been made to this end, it seems necessary to determine still more precisely the behaviour of iodine (or its compounds) from its origin to its release into the atmosphere.

## 2.5. Evaluation of reactor accidents

A paper by HILLARY and TAYLOR /11/ describes the reproduction in the laboratory of accident conditions in a SGHWR. Fission products were released from fuels by heating to failure at 1 000 °C in a current of steam/argon. The authors arrive at the conclusion that the extent of Xe-133 and I-131 release depends on irradiation conditions. Finally they propose a series of factors to predict the release of total iodine or a penetrating species of iodine on the basis of the measured activity of rare gases. These factors are repeated below :

Factors to determine
the release of

|  | total iodine | penetrating species |
|---|---|---|
| $\dfrac{Xe-133}{I-131}$ | 7 | 70 |
| $\dfrac{Kr-85}{I-131}$ | 70 | 700 |

The burn-up has an effect on the total quantity of iodine formed which is considered as being stable (I-127 + I-129). It has been suggested that less methyl iodide would be formed, the greater the total iodine quantity present. But, in fact, is it not rather the proportion of organic impurities relative to iodine which ultimately governs the reaction and controls the final quantity of penetrating species ?

In the course of this chapter dealing with the physico-chemical species of iodine, it is observed that this point has always seemed crucial. The origin of methyl iodide, and the nature of those species of iodine which are more penetrating, still have to be firmly established.


3. THE AGEING OF IMPREGNATED CHARCOALS

3.1. How does ageing affect the traps ?

A most serious problem is posed by the change in the retention properties of charcoals in respect of iodine or methyl iodide in the course of time. It is this phenomenon, which is not sufficiently well known, which causes a trap in either continuous or intermittent operation at a given moment to become less efficient than was measured initially. At all events a plant operator needs to know what retention efficiency he may expect for the different species of iodine. For this reason periodic in-situ inspections of the traps are carried out. The importance of these ageing phenomena and the in-situ inspection of traps is such that it provided a fitting title for our Seminar.

The paper by L.R. TAYLOR and R. TAYLOR /14/ dealt specifically with the study of ageing. British research on this topic in progress for several years has been aimed at reproducing changes in the efficiency of a charcoal bed impregnated either with potassium iodide or with triethylenediamine, both dynamically and statically.

An ageing index is used to express dynamic ageing in terms of the number of times a volume of air equal to the volume of the charcoal bed was passed through the trap. It is more conveniently expressed as the number of air changes.

One can in the case of $CH_3I$ define an index of performance K equal to $\log_{10}$ of the decontamination factor DF *) divided by the stay time t

$$K = \frac{\log_{10}DF}{t}$$

where

$$t = \frac{\text{charcoal bed volume}}{\text{volume flowrate}}$$

The authors arrive at the conclusion that this index of performance can be expressed as a function of the number of air changes to which the trap is exposed, by relationship of the type :

$$\log_{10}K = \log_{10}K_0 - C_1 N$$

where $K_0$ is the initial index of performance of the trap
$C_1$ is a constant
N is the number of air changes from the start of in-service life.

In the same way this index of performance would be linked to the age of the adsorbent by a linear law in the form :

$$\log_{10}K = \log_{10}K_0 - C_2 \tau$$

in which $\tau$ is the age of the charcoal in weeks
$C_2$ is a constant.

The constants for the two equations (for specific impregnated charcoals in air) were determined both in laboratory and plant tests under dynamic and static conditions. These equations may be combined to give :

$$\boxed{\log_{10}K = \log_{10}K_0 - 0.3 \times 10^{-8}N - 1.3 \times 10^{-3}\tau}$$

## 3.2. Discussion on ageing

One of the first questions which comes to mind is the origin of this ageing. While the expression suggested above accounts for the extent of the phenomenon in the course of time, it in fact does not explore the causes. If

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*) DF or decontamination factor is the reciprocal of the fractional penetration.

we examine an impregnated charcoal unit in its original packing which keeps it airtight, ageing is nevertheless observed. Examples can be found /15/ in which charcoal has deteriorated to a greater extent than one would expect from the above formula. It has been suggested /14/ that this ageing may be produced by a substance contained in the charcoal base itself, and sulphur is suspected as a possible cause. Another explanation could be recrystalliza- tion of the impregnant.

Dynamic ageing of charcoal also suggests the possibility of slow oxi- dation, resulting from the oxygen in the air.

However, it seems necessary to distinguish between ageing and poiso- ning in order to apply the above equations. These equations can only repre- sent ageing if the air circulating over the trap has a standard composition and if there is no major contaminant in the traps — oil, vapours of solvents etc. — thus the word ageing may be misleading if not precisely defined.

To sum up the situation, bearing in mind that the trap is certain to age and furthermore is exposed to "poisons", it is preferable to dimension the traps generously, so that they are initially capable of a performance much higher than the minimum required by licensing specifications. The final cost of the operation must obviously be borne in mind, but under no circumstances is it advisable to be satisfied with minimum standards of performance.

CONCLUSION

As a conclusion to the deliberations of the participants which formed the basis of this chapter, it would be useful to stress the main points, which seemed to emerge throughout this session and which might merit further studies in the future.

1. Definitive characterisation of the penetrating species of iodine (HIO, HIO$_3$) involving advanced analytical procedures — mass spectro- metry, for example.

2. The processes of formation of these penetrating species. It has been shown that a possible formation process of methyl iodide — to take only this compound — could be by radiolytic reaction within

the gaseous phase. Future work in the laboratory, under realistic conditions such as might be encountered in a reactor, may doubtless either invalidate or confirm this hypothesis and perhaps even quantify more accurately the composition of the gas-borne species to be filtered.

3. Studies on the problem of the ageing of sorbents will obviously take a long time. It is suggested that an attempt be made, in the near future, to try to collate all the results obtained from in-service experience, for example, and, if feasible, attempt to analyse the data so obtained, referring, for instance, to the index of performance proposed by the British authors.

A first step in this direction has been taken at the Karlsruhe Seminar, where a comparison of the techniques used in various laboratories has been initiated; this is to be followed by further comparisons with various sorbent materials.

The European Communities have proposed a further meeting in a few years' time on the subject of iodine traps. Perhaps, on that occasion, new factors will emerge, at present unforeseen ?

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## DESIGN ASPECTS *)

J.J. Hillary

INTRODUCTION

Albeit in the context of a seminar on Iodine Filter Testing, it
is undoubtedly true that the fundamental requirement of the sorption
unit of an iodine trapping plant is good design. In an ideal situation,
if this is realised, then testing is carried out merely to prove the
performance and to ensure that it is maintained above an acceptable
level throughout its service life. In reality this is not by any means
always so and there are many examples of cases in which testing has
served principally to highlight design, as well as manufacturing, in-
stallation and maintenance defects. There is in practice an inter-
action amongst these factors which must be appreciated and unfortu-
nately very often experienced before a plant - and its design - becomes
acceptable.

The essential information which must be available to provide a
complete basis for design may be conveniently considered as answers
to the questions:

    What is the plant required to trap ?
    Under what conditions will it operate ?
    What performance is required ?
    How can these requirements be best achieved within the
    limits of existing scientific and technical knowledge ?
    What are the economic constraints ?

The nature of this information will change by different degrees
depending upon the various duties for which the plant is required -
once-through reactor blowdown or recirculation, containment ventila-
tion or clean-up, and also on nuclear reactor type; stand-by or continuous
operation with flowing gas; hot cell or fuel reprocessing plant duty.

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*) Bibliography see p. 73

In the context of the present seminar it is useful to ask the questions : what further information and work programme are required to eliminate current design problems and how far can existing designs be said to be satisfactory ?

One of the sessions of the seminar was devoted to design aspects of iodine sorption plant. In addition the other sessions of the seminar, together with the discussion periods, included many additional references to design and in this brief report an attempt is made to summarise design aspects material derived from the whole of the meeting. In particular, there was a considerable feedback from plant testing experience since the latter, in some instances, brought to light design defects which could then be dealt with. It should also be borne clearly in mind that the seminar was devoted almost exclusively to the trapping or sorption of vapour forms of iodine-131. Nevertheless, even if not given undue emphasis here, the same trapping plant has to deal with other fission products and with other gas-borne species, principally in particulate form. Consequently, in addition to the sorption bed which controls the release of iodine and its compounds, the plant will include at least one high efficiency particulate filter of the HEPA or "absolute" type. Furthermore, in many applications there will also be a requirement for a device to control free water droplet removal.

In an introduction to the design of iodine sorption plants attention should be drawn to a U.S. report /16/ which is one of the few available documents on this subject.

It has been endeavoured to classify the design information which was presented at the meeting in terms of design requirements (species to be trapped, sorption material and engineering factors), design evaluation and applications and operational experience.

DESIGN REQUIREMENTS

## Iodine Species

Little new of note was reported here, although work continues in various laboratories. During the discussion some evidence was given for further penetrating species of iodine and experiments are in hand to confirm the nature of these compounds. Gas chromatographic techniques are also being developed to examine the form of iodine released during fuel reprocessing operations at WAK *), Karlsruhe. A cautionary note was sounded in interpretation of data derived with the latter technique, that experimentalists must ensure by careful work that species are not changed or formed by the application of such an analytical device particularly at low mass concentration.

A British paper /11/ reported the results of a few out-of-pile tests which indicated that the proportion of penetrating iodine, probably methyl iodide, released from Zircaloy-clad $UO_2$ fuel into steam at 1 000°C might be quite small.

In an interesting theoretical paper /8/, BARBIER concluded that a precursor of iodine-131, tellurium-131, might be important in determining the transport behaviour of the former isotope. It is not clear whether there is any experimental basis for this observation and it will be of interest to see if this is confirmed in the future.

In U.S.A. and to some extent in Germany the data on the distribution of released iodine species have been interpreted to give definitive guidance to plant designers and operators. In the U.S. they have been issued in the form of a USAEC Regulatory Guide /17/. Clearly there is a need for authoritative documents of this type, so that the designer, manufacturer, and supplier may have the necessary basic information. It is nevertheless important that too much detail is avoided and that such data are reviewed and updated from time to time.

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*) Wiederaufbereitungsanlage Karlsruhe

## Sorption Materials

Work on the development of sorption materials for iodine and its vapour compounds continues in a number of countries. No new materials were reported and the principal points for attention concerned non-flammable alternatives to charcoal, in-service deterioration of charcoal ("ageing") including poisoning aspects and the evaluation of high radiation effects.

Disadvantages of charcoal are its relatively low desorption temperature and its ease of oxidation in air at elevated temperatures which may lead to ignition problems. Relatively inert, non-flammable alternative materials have been developed which are suitable in many respects for trapping iodine and its compounds and these have been based principally on silver impregnated materials such as zeolites. The principal disadvantage of silver coated sorbents is their high cost compared with, for example, impregnated charcoals. Also operational experience with these new materials is presently limited.

A French paper /18/ described work on the development of silver impregnated zeolites for trapping purposes at elevated temperatures and during the discussion it became clear that these more expensive materials are likely to be restricted to high temperature applications. It appears that they have reached the stage of being manufactured in bulk for pilot-scale evaluation.

For fuel reprocessing plant use, which would include in the future I-129 as well as I-131 removal in presence of large gas-borne concentrations of nitric acid and nitrogen oxides, other silver impregnated materials have been developed, particularly in Germany, and a paper was presented describing work with solid sorbents /19/ (as opposed to liquid types based on aqueous nitric acid or mercury salt systems) which may be more suitable for handling and ultimate storage.

There was considerable interest and discussion on the question of the effect of in-service conditions on the performance of charcoals. A British paper /14/ described work in static and flowing air, both in the laboratory and in operating charcoal bed sorption plant on the ageing of KI and TEDA impregnated coalbased charcoals with respect to their perfor-

mance with methyliodide in the standard high humidity test. This work indicated that at least in the prescribed conditions used in the experiments a relatively simple formula could be applied to describe the deterioration rate and thus make a prediction and allowance for this factor in plant design. In discussion it was pointed out that this work was continuing on as broad a basis as possible to collect data under many different operational conditions.

In contrast to this, other European, German in particular, /15/ and U.S. experience seems to indicate variable charcoal performance both fresh and in respect of deterioration rate. Life times in service varying from 2 months to several years were quoted. In some cases poisoning by identified compounds was at least partly reponsible for this deterioration.

It is to be anticipated that these apparent differences in results should be capable of explanation in the future assuming that this work continues and various effects or mechanisms can be separated and identified. Clearly it is an important aspect of sorption technology meriting further work both on charcoals and newer alternative materials. Additionally, attention should be given to storage conditions, in-plant as well as in-drum, to lengthen in-service life, particularly for stand-by situations.

During the discussion periods, in the particular context of LWR safety, much reference was made to the requirement for investigation of the effects of high radiation on charcoal performance, in simulation of the immediately post-DBA *)situation . This aspect, together with simultaneous and combined effects of oxidative heat production and gas (air) flow on ignition characteristics and effects of test materials like D.O.P. **), used for HEPA performance testing, and freons, is covered by the very comprehensive programme of development work currently being carried out in the U.S.A. /20/ /21/. It is understood that consideration is also being given to the incorporation of some European sorption materials into the U.S. programmes.

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*)  Design Basis Accident

**)  Dioctylphthalate

There was some discussion of the need for specifying the various physical characteristics of charcoals for use in iodine trapping plant. For example, quite close tolerances recognized to be wasteful for the manufacturer are placed upon particle size distribution in USA /17/ /22/ so that performance with methyl iodide, plant pressure drop and dust content may be properly controlled. It also appears that some European countries, e.g. Germany, are making progress towards closer definition of these parameters. Additionally, there are also requirements for manufacturers to be asked to supply samples of charcoal representative of the batch loaded to the plant so that they can be tested with methyl iodide to confirm their performance both fresh and after periods of simulated in-service time.

## Engineering Factors

Given a comprehensive knowledge and understanding of the gas-borne iodine compounds which require trapping, the conditions under which the iodine sorption plant will operate, a well defined objective of performance derived from a safety assessment and a suitable trapping material with adequate permanent retention properties, it then remains to undertake the chemical engineering task of designing the plant.

The principal requirement here is to ensure that all the gas which requires cleaning contacts the sorption material efficiently. Thus a particular iodine sorption unit — which will normally be based on a solid sorbent — must be so designed as to incorporate the minimum of seals and any devices which may allow gas to by-pass the sorbent and carry with it untreated iodine.

The whole plant section, or duct, must therefore be completely filled with sorbent so far as this is possible. This ideal however is in practice difficult to achieve, for it frequently conflicts with other requirements such as refill capability, maintenance, sampling and instrumentation.

Of other design considerations, the more important include flow direction (to avoid fluidisation, settling), sorbent staytime (to achieve maximum performance), iodine loading, available pressure drop, sorbent retention arrangements (to ensure especially in shallow layer designs that channelling cannot develop), inclusion of facilities for

plant testing and removal of typical sorbent samples for laboratory assessment.

As noted earlier it is a feature of the U.S. approach in this field that information of the type presented in the Burchsted-Fuller handbook /16/, up-dated and extended in some respects, is being incorporated into documents /17/ which give guidance to the U.S. air cleaning industry on the design of suitable plant for the control of fission product iodine release from nuclear facilities. Two further references given in the above document /17/ appear to be of special interest covering the design of high efficiency gas phase iodine sorption units /23/ and the supply requirements - which again represent defined design objectives - for activated carbon sorption materials /22/. The document contains much information of value to the designer and includes sections on system design criteria and qualification testing, maintenance requirements and laboratory testing criteria for charcoal.

These factors will be discussed in the following section in the context of other papers presented at the seminar together with points made during the discussion periods.

DESIGN APPLICATIONS AND OPERATIONAL EXPERIENCE

Contributions on a wide variety of sorption unit types were presented at the meeting, viz.: for gas-cooled reactor discharge (high pressure) and recirculation or ventilation plant, water-cooled reactor trapping plant, hot-cell and fuel reprocessing duties. Once-through and recirculating designs were included, both deep and shallow-bed types. Flow direction and other design parameters included many variations.

The session on design aspects of iodine sorption plant comprised five papers, two of which concerned principally sorption materials development either for fuel reprocessing purposes /19/ or for specialised high-temperature application /18/. Of the three remaining papers, one by HERRE /24/ (Germany) related to engineering design aspects of fuel reprocessing plant units. The presentation by STRAUSS et al /25/ (Germany) described two designs, a ring-type system and, more importantly, a deep-bed horizontal-flow system with convenient gravity-flow charcoal filling and emptying

arrangements. It is perhaps of special significance that the latter unit was stated during discussion to have given consistently very good in-situ test performance. The other paper by PASSANT /26/ (Britain) described a deep-bed vertically downwards-flow system which was installed in the "Magnox" type nuclear power stations. This design had given variable in-situ test performance results /27/ but with careful attention to flanges, seals and installation had been shown to be capable of giving good performance. PASSANT also described a similar design for commercial AGR stations.

Other papers, particularly in the test experience session, described designs associated with :

    a) the British Windscale AGR and several hot cells /28/ incorporating a variety of deep-bed design concepts most of which when applied had given initially poor in-situ test results; by attention to seals and other by-pass problems, and to one instance of extensive poisoning, these plants had been improved and the performance essentially restored to a satisfactory level;

    b) the British Winfrith SGHWR /29/ comprising a quite large-capacity (300 $m^3$/min) down-flow design based on deep-bed (10 cm) but relatively large diameter open-tray concept which had been shown to perform satisfactorily;

    c) various Italian designs /30/ referred to below; and

    d) other European designs generally of the deep-bed type, German /31/ French /32/, shallow-bed, Dutch /33/, Belgian /34/ and Swedish /35/ which had usually given satisfactory in-situ test performance but with, in some cases, reported leakage and settling (by-passing) problems : in general, little detailed design information was given in these latter papers, thus it is difficult to comment except in broad terms.

An additional feature of the design session of the meeting was the presentation of slides by ZAVADOSKI (U.S.A.) to illustrate the interaction of other items of nuclear power plant on iodine trapping plant installations in the U.S.A. Some of the points made were :

a) the inadvertent omission of water seals in pipes permitted by-passing of sorption units;

b) seals for components were non-uniformly loaded or not held down firmly enough, giving by-passing problems;

c) removable charcoal samples were merely suspended in an air stream and thus were not experiencing typical in-service flow conditions; and

d) access for sorption plant examination and maintenance was often quite restricted by other plant items.

These comments and illustrations have recently been extended in a further paper by ZAVADOSKI et al. in 1974 /43/.

One of the principal points for discussion was the question of bed depth. Practice in Europe, with few exceptions, has been to adopt a relatively deep sorbent bed (normally 10 cm or more) - on which many satisfactory in-situ test results were reported - as the basis for design with the main objective of reduced risk of channelling but usually with the disadvantage of higher pressure drop. In contrast, U.S. practice has been based on a relatively shallow-bed depth (5 cm or less) particularly in respect of LWR secondary containment clean-up where very large flow-rates of air (5000 $m^3$/min) are required.

It was noted in discussion that a deep-bed design is presently being installed in one plant in the U.S.A. and, on the other hand, consideration was being given to the use of shallow-bed types in Britain, for large flow ventilation duty . An Italian paper /30/ on operational test experience quoted results on both shallow and deep-beds which indicated variable efficiency, but there was no explanation for this.

It was apparent that no comparative test data, deep-bed versus shallow-bed, were available in U.S.A.  However from German experience it was clear that almost invariably the shallow-bed filters give poorer results than deep-bed filters of vessel type.

Undoubtedly more work needs to be done to evaluate this design variable on both pilot and full-scale and it is understood that experimental

studies are proposed in Britain.

Both in the presentation of papers and during discussion a clear distinction emerged between British experience and that in other European countries. The former designs had shown, apart from individual cases of poisoning, principally problems associated with by-pass leakage - i.e. inability to get all the gas being treated to contact the sorbent - whereas in the latter cases there was relatively much more pre-occupation with problems of the sorbent material itself, particularly in respect of variable in-service performance and poisoning or radiation effects.

Test experience also drew attention to a further point in the area of definition of objectives. British experience /28/ indicates that it is difficult in practice to achieve a performance better than a D.F. *) for methyl iodide of $10^3 - 10^4$ or, with care, a little higher /27/. It is arguable therefore that this should represent a realistic objective for the purpose of safety assessments.

Further to the information presented on the continuing development of non-flammable alternative sorbent materials, there was a stimulating discussion on the potential charcoal ignition problem from a plant design and operation viewpoint. This was mostly in terms of clarification of present U.S.A. practice. The objective is to prevent the occurrence of charcoal ignition; there is some evidence that once it has taken hold it is difficult to control . Water sprays are incorporated into the design to provide additional cooling to the sorbent, and it appears that work is continuing to define operating limits, e.g. critical water-flow. What was not clear, however, was the extent to which the effect of flooding of the charcoal on its iodine removal performance was being taken into account.
These sorption plants are duplicated so that flowing conditions can be ensured (and, thus, better heat removal) by the use of alternative fans and cross-over lines.

The difficulties of designing a suitable system for monitoring the sorbent material during service were also discussed at some length.

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*) D.F. or decontamination factor is the reciprocal of the fractional penetration.

The alternative methods are :

a) to simulate in-service life in the laboratory, probably only directly relevant for plants on stand-by duty;

b) to incorporate **removable** samples into the main sorbent bed as typified by **British practice at Windscale** /28/ ;

c) to arrange a sample or samples on a by-pass line parallel to the main plant, taking a proportion of the main gas flow, as **applied** in Germany and in France;

d) to incorporate a removable plant section of the pleated "V" type unit; or

e) after gaining access to the bed to take samples by hand /29/.

Each of these methods has certain **dis**advantages and there is probably no ideal solution when the number of samples required for adequate **monitor-** ing is taken into account. Nevertheless, a good deal can be done in this manner and continued experience will show how satisfactory, compared with samples taken directly from the plant at end-of-life, these methods prove to be. The limited British experience here /14/ /28/ with one type of plant and charcoal indicates promise of a solution but this will have to be judged against experience presently being gained in a wide variety of plant applications.

## SUMMARISING REMARKS

In summary there was, in the limited context of the design aspects which were considered, a useful discussion of a number of points. It is clear that there are continuing problems, both on the requirements of the sorbent material, e.g. in-service deterioration characteristics, develop- ment of non-flammable alternatives to charcoal, but perhaps more so with regard to plant engineering. A large number of differing designs and appli- cations were described, though many in insufficient detail. Experience in testing these various designs in-situ gave rise to variable results, some very good, but some poor. However, in most cases the latter can be overcome by further attention to design (and construction, installation, maintenance)

\o eliminate by-pass routes in particular and, in the main, good or adequate performance restored. It appears to be necessary at an early stage however to concentrate upon fewer designs so that a point may be reached quite quickly at which greater confidence can be placed upon a particular design concept.

Specific design aspects which appear to merit continuing attention comprise :

a) Elimination of routes for by-passing of the sorbent.

b) Sorbent sampling arrangements to enable the satisfactory monitoring of the sorbent, in-service, to be carried out.

c) Establishment of rules or guidelines for the assessment of allowances for adequate margins for sorbent ageing or poisoning and other factors of uncertainty.

d) The interaction of other plant items and of factors such as maintenance, sampling and testing requirements on design.

e) Studies of the properties of sorbent materials, including :

(i) In-service deterioration due to poisoning or ageing effects

(ii) Radiation effects

(iii) Stability with respect to oxidation and desorption.

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TEST METHODS AND OPERATIONAL EXPERIENCE *)

J. G. Wilhelm

## Introduction

Normal safety procedures designed to ensure the availability and reliable performance of important components of engineered safeguard systems in nuclear technology include the testing of iodine sorption materials in the laboratory and in-situ testing of iodine filters. Such tests are carried out in virtually all countries which have nuclear plants equipped with iodine filters. Test results are not readily transferable, however, since the methods and test conditions used are not known in sufficient detail, and no attempts have been made as yet to lay down international standards. This causes problems not only for the manufacturer of iodine filters who wishes to sell his products on the international market and for the buyer and the expert who have to accept or give an opinion on the performance of the filters, but also for the research worker, who cannot readily compare the values measured in his own laboratory with other data, and is therefore always in some doubt as to the validity of his results. The seminar on iodine filter testing provided an opportunity for detailed consideration of the various testing methods in the papers presented and the exhaustive discussions which followed, with a view to finding a common basis for comparative measurements.

## Test agents used to measure the penetration of iodine sorption materials and iodine filters

All the reports (presented by authors from Germany /36/ , the United Kingdom /37/ , France /38/, Italy /39/ , the Netherlands /40/, and Sweden /35/) mentioned I-131-labelled methyl iodide (a mixture of $CH_3I-131$ and $CH_3I-127$) as a suitable test agent both for laboratory tests of the iodine sorption material and in-situ testing of iodine filters, and reported on the relevant experimental techniques. Some papers also referred to the use of labelled elemental iodine. The properties of these two test agents were compared in several papers, e.g. /37/ , showing that methyl iodide has certain definite advantages for in-situ testing over elemental iodine, namely a simpler production method, easier handling, higher vola-

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*) Bibliography see p. 73; German version see p. 59

tility and relatively high chemical stability. The use of elemental, la-
belled iodine as a test agent instead of methyl iodide is usually only essen-
tial for in-situ testing where the leaktightness of iodine filters loaded
with unimpregnated charcoal is being tested. This type of sorbent, which
does not remove organic iodine compounds to a satisfactory degree, should
not be used in nuclear installations. The sorption of elemental iodine on
surfaces, which complicates in-situ testing among other things, can be
reduced by depositing inactive elemental iodine on surfaces before the
in-situ testing is carried out, as was reported in references /38/ and
/32/.

During the discussions, great interest was expressed in a compa-
rison of in-situ testing with methyl iodide and the test method introduced
in the USA entailing the use of freons /41/. Being inactive, freons require
no safety measures for radiological protection. However, freon test methods
have not become popular in Europe, and only two papers, references /39/
and /30/, gave some details of them and of the equipment used. The expe-
rimental effort required seems disproportionately high compared with the
methyl iodide-131 testing method, because it is necessary to carry out pre-
liminary experiments and measure very small concentrations of freons quan-
titatively by gas chromatography. Analysis using methyl iodide-131 requires
only one measuring device, which is a normal part of the basic equipment
of a radiological protection laboratory in nuclear plants.

In the lively discussion on the use of methyl iodide-131 and the
freon testing method, the following points were considered :

1. Comparison of the time needed for the filter testing.

   The two methods of testing for leakage were said to require about
   the same amount of time, excluding the time needed to manufacture the
   labelled methyl iodide.

2. The possibility of repairing a leak immediately after it has been dis-
   covered during the in-situ testing.

   If filter bank systems with charcoal filter cells are used, there
   could be certain advantages in using freon as a test agent in that it
   will not cause radioactive contamination of the filter. In the case of
   testing of iodine filter units which have filter housings or such filter

banks, which permit use of the bag changing technique, or in the case
of deep-bed vessel-type filters which can be loaded with charcoal through
charging inlets outside the contaminated area, contamination of the
filters during the in-situ testing is not a problem. When filters have
been contaminated during normal operations, the additional contamination
caused by testing with methyl iodide-131 is of little account.

The material presented at the seminar was not extensive enough to
allow a comparison of test results using freons and methyl iodide-131 for
in-situ testing. Nor did any clear picture emerge from the discussions.
Even allowing for the fact that freon testing is purely designed to detect
by-pass mechanical leakage and does not provide indications of fission
product iodine retention in the charcoal, as does the methyl iodide-131
test, the interest shown in a comparison of the results of the two proce-
dures is understandable, particularly as freon testing in the USA has been
approved by the USAEC /17/ . It would seem that additional work in this
field is vital, including a check on any possible poisoning caused by the
freon in the charcoal.

## In-situ testing of iodine filters with labelled methyl iodide

It was evident from the papers presented that there are only minor
differences in the application of the in-situ testing method with methyl
iodide-131 in the various countries, and that these differences relate to
the methods used to manufacture the test agent, the number and design of
the samplers upstream and downstream and different sampling times during
the testing. All reports agreed on the use of test agent activities between
1 and 100 mCi methyl iodide-131; the activity required in each case is
determined by the flow rate through the filter system being tested, the
sample flow rate for measuring the activity and the detection threshold
of the measuring equipment. It is important to establish that the risk of
an appreciable release of radioactive test agent can be excluded by pre-
liminary testing with a low activity source.

A discussion then ensued as to whether the same charcoal should
be used for the sampling during the in-situ testing as in the iodine filter
under test, or whether it would be better to use charcoals of very high
efficiency in the samplers (e.g. charcoals of very small grain size which

cannot be used in iodine filter plants). By using charcoal from the origi-
nal batch in the sampler, a direct comparison can be made between the effi-
ciency of the unused charcoal (when a multi-stage sampler is used) and that
present in the iodine filter which has aged during operation and may be
also poisoned. Against this advantage, however, there is the fact that the
flow rate through the sampler must be adjusted according to the air veloci-
ty in the main filter, so that the already large ratio between the flow
rate through the iodine filter, usually several thousands or tens of thou-
sands $m^3/h$, and the partial flow through the samplers which is in the region
of 0.1 to 10 $m^3/h$ becomes even less favourable. Additionally, this method
of testing the sorbent material is less sensitive than a laboratory test.

The results of in-situ tests using labelled methyl-iodide can also
be difficult to interpret. One problem referred to in the discussions was
the apparently unavoidable slight contamination of the test agent with
still more penetrating iodine compounds than methyl iodide. When deep-bed
filters of very high efficiency were tested, the activity retained in the
activated charcoal sampler down-stream of the iodine filter was often un-
evenly distributed, instead of showing the normal separation profile, which
can be described as an exponential function. The distribution suggested
highly penetrating iodine compounds rather than the normal retention beha-
viour for elemental iodine or methyl iodide. In such cases, the result of
the test depends not only on the total attributable to mechanical leakage
and penetration of elemental iodine or methyl iodide, but also on the pro-
portion of highly penetrating iodine compounds in the test agent. The
possibility of misinterpreting test results can largely be excluded by
careful examination of the retention profile of the test agent activity
in multi-stage down-stream samplers. Using elemental iodine as a test
agent, certain workers /33/ have established a ratio of elemental iodine
to other iodine compounds in the exhaust air varying between 1 : 15 and
1 : 670; an arithmetical mean of 125 was calculated. When methyl iodide
was used, this ratio of methyl iodide to other iodine compounds was
1 : 2 x $10^{-4}$ to 1 : 0.1.

In this connection, the results of measurements with May-Pack-type
samplers down-stream of an iodine filter through which the exhaust air from
a hot cell was filtered were particularly interesting /34/ . Iodine compounds
were observed to behave very differently as regards removal behaviour, de-

pending on the reagents used in the hot cell for the separation of I-131 from irradiated tellurium oxide. Similar measurements showed that retention efficiency apparently depended on the iodine concentration /31/ .

The validity of in-situ tests with labelled methyl iodide was also discussed in connection with the conditions under which the iodine filters operate :

In-situ tests can usually only be carried out under the normal operating conditions of the iodine filter unit to be tested. The degree of penetration measured when labelled methyl iodide is used as the test agent can only be considered to be a sufficiently conservative indication of the performance of the iodine filter when exposed to a fission product iodine mixture of unknown composition if the test conditions are not essentially different from the most unfavourable operating conditions. In particular, when the penetration to be expected under reactor accident conditions is assessed, the effect of the relative humidity of the air, which may be markedly increased, must be taken into account. The accuracy of an extrapolation of the penetration values measured during in-situ tests for increased air humidity is highly problematical since :

1. It cannot be ensured that the charcoal in the iodine filter is in adsorption-desorption equilibrium with the water-vapour content of the incoming air. Measurement of the relative air humidity, which is easily carried out during the in-situ testing, does not permit any correlation between air humidity and penetration.

2. The relationship between the penetration of the charcoal and air humidity cannot be expected to be the same as it is in laboratory tests involving unused charcoal.

3. The degree of penetration indicated by the in-situ testing reflects the total leakage rate attributable to mechanical leakage and the penetration of the charcoal, and the importance of individual effects cannot be ascertained without additional effort.

It was pointed out in the papers and discussions that considerable ageing and poisoning can be observed even during the in-situ testing with labelled methyl iodide under normal operating conditions (see, for example, details given in references /35/ and /15/),but that it is not possible to

make any definite statement regarding the penetration following an accident or regarding the condition of the charcoal without additional laboratory testing of representative activated charcoal samples from the iodine filter. It is not always possible, however, to remove samples from the filter, and removal can in any case cause leakage if not properly controlled.

It was reported in one paper /32/ that the values measured during the in-situ testing bore no relation to the results of the laboratory tests. The difference was attributed mainly to mechanical leakage and dust, which is a possible explanation. The combination of a number of effects on an iodine filter after a serious accident can lead to activity releases with consequences not apparent either from the results of the in-situ testing or from laboratory tests. A supplementary type test for emergency iodine filters under simulated accident conditions would therefore appear to be necessary. In reference /42/ a suitable filter test facility is described.

Laboratory testing of iodine sorption material

All the papers on the testing of activated charcoal in the laboratory showed agreement on the choice of labelled methyl iodide as the test agent. In a few cases, additional tests were carried out using labelled elemental iodine. The kinds of equipment described can all be used to test iodine sorption materials in air or gas of high relative humidity (R.H.), although the apparatus and instruments provided vary considerably, and it is possible that these differences lead to different degrees of retention being measured for the same activated charcoals under comparable conditions. The relative gas humidity proved to be the most difficult parameter to fix and measure, especially when measurements were carried out in the region of high air humidity ($\geqslant$ 95 % R.H.).It was apparent from the discussions that the various European laboratories are extremely interested in comparative testing, and participants welcomed the fact that the Commission is prepared to organize an intercomparison programme. It will be more appropriate to comment on the various types of laboratory test apparatus when the results of comparative testing are available.

It was also agreed that it was essential to test the retention efficiency of the charcoals with respect to labelled methyl iodide in order to assess their suitability for use in iodine filters. None of the papers dealt with the testing of other properties of activated charcoals. It was

apparent from the discussions that systematic measurement of the grain-size distribution, the internal surface, pore size and distribution, porosity, hardness, impregnation etc. are carried out almost exclusively by the manufacturers of charcoal and, to a much smaller extent, by filter manufacturers. Those laboratories which do measure the retention efficiency of the charcoal seldom measure the other properties.

The grain size is a particularly important factor affecting the retention efficiency of a specific type of charcoal. It was pointed out during the discussions that a definition of the maximum and minimum grain sizes has not in itself proved sufficient. The percentage distribution of the various grain sizes within the given limits must be standardized. In a few countries therefore the proportion of the charcoal within closely defined particle size ranges must be carefully controlled, thus largely excluding any alteration of the retention efficiency on the basis of grain-size distribution.

The papers and discussions showed that laboratory tests on iodine sorption material using labelled methyl iodide must be carried out under carefully selected and controlled conditions in order to :

1. Check the suitability of unused charcoal batches as charged to the iodine filter, because the efficiency of different charcoal batches even of the same type from the same manufacturer can vary considerably.

2. Analyse quantitatively in-service ageing and poisoning effects in order to determine the overall effect on the performance of the charcoal under the most severe operating conditions.

Point 2 is also of importance with respect to the required frequency of routine testing.

## Frequency of in-situ testing

Several papers, for example /28/ and /15/, dealt with the required frequency of routine iodine filter plant testing. There was no unanimous agreement, intervals between tests varying between about two months and two years. The importance attached to routine tests was reflected in the large number of contributions to the discussions.

The following overall picture emerged :

The efficiency of iodine filters is quickly impaired by external influences, particularly substances such as oil and organic solvents. Routine checks are required if they have been exposed to the effects of harmful substances or after operation under extreme conditions of pressure, humidity and temperature. It is not certain, however, that the full effects of such substances can be recognized in practice.

Any predictions of the extent of contamination and poisoning of activated charcoal filters will entail precise knowledge of the amount and nature of the contaminants and the time they have been accumulating in the filter. Often, such predictions cannot be made, or cannot be made with the required accuracy. An unexpectedly rapid decrease may therefore occur in the efficiency of iodine filters which are in continual use or which are brought into operation after minor incidents such as may be expected to occur rather frequently during reactor operation and which lead to minor activity releases possibly accompanied by a release of steam. The ageing of charcoal, which may be determined experimentally, independently of any abnormal effects, as in the case of enclosed samples, is taken to have a basically much smaller effect on performance. The overall result, therefore, incorporates some uncertainty as to the achievable efficiency at any particular time, and this uncertainty cannot completely be eliminated by frequent routine tests.

The necessity for routine tests depends on the way in which the filter works, external influences, the design of the iodine filter, and in particular the excess of charcoal added (to take account of ageing, poisoning) and the quality of construction.

If all these points are taken into account, the conclusion is reached that it is not possible to lay down any definite rules as to how often iodine filters should be tested (for example see references /28/ and /40/). The test frequency should be determined for each individual case on the basis of an evaluation of the consequences of such a deterioration of performance and, where possible, on the basis of experiments, including specific ageing experiments /36/. In principle, iodine filters should be designed to accommodate an additional quantity of charcoal to compensate for ageing and poisoning. The cost incurred would be low in comparison with

the expenditure for the additional testing which would otherwise be required. If the design of the filters used is appropriate and reliable, fewer in-situ tests will be necessary, since samples of the charcoal from the filters can be examined in the laboratory between tests.

During the discussions it was pointed out that by systematically separating emergency iodine filters from those for normal operating conditions, an increased level of safety could be obtained, with respect to the performance of the filters in case of accidents. This solution would largely exclude the preloading of iodine filters which in the event of any accident have a critical role to play in limiting environmental contamination. It would also make it possible, where the design has proven reliability, to rely on the performance of the filters with sufficient confidence with a limited test frequency. The division of the filters into those two categories of application presupposes a clear definition of the concepts of emergency and normal operation. As the discussions showed, ideas on that subject vary considerably and the design of the individual reactor and ventilation systems must be taken into account when drawing the dividing line.

## Provision of charcoal samples from the iodine filters

If no special design features are included for the removal of charcoal samples from iodine filters, it is usually not possible to obtain representative samples for laboratory testing. Moreover, sampling may cause leakage, especially when the filter cells have to be taken out for the removal of the representative charcoal samples. The leaktightness of the replaced filter cell can often only be verified by further in-situ testing. In such a case, the effort involved in obtaining a representative sample of charcoal is too large. Difficulties can also occur in the case of deep-bed vessel-type filters because they are usually designed in such a way that it is not possible to remove charcoal samples which are representative of the whole bed depth.

Several papers referred to the use of equipment in which a proportion of the flow to the main charcoal filter is diverted through a sample holder containing charcoal taken from the original charge of the main filter. This means that representative charcoal samples can be obtained without access to the iodine filter itself. One disadvantage of passing the air

through the samples in the by-pass is the increased probability of mechanical leakage. The by-pass sample holders must conform to the same standard of leaktightness as the iodine filter itself. Since every additional by-pass increases the risk of a leakage, their number, and thus the number of available charcoal samples, must be strictly limited. Once they have been tested, charcoal samples are not usually replaced in the by-pass sample holder. In view of the uncertainty regarding the test frequency, there is no guarantee that the limited number of samples available will be sufficient to permit testing throughout the service life of the filters.

During the discussions, various designs were mentioned which allow the air to pass through charcoal samples in the by-pass. However, since no complete data are available on the number, design and leaktightness, no comparative assessment can be made at the present time. It should also be pointed out that the by-pass samplers used in the Federal Republic of Germany, which are known as "control filters", must ensure separation of the activated charcoal into at least two consecutive beds. Thus any poison migrating down-stream through the bed will be detected in the laboratory and the remaining depth of the unaffected charcoal can be measured at each laboratory test. Experience to date has shown that contaminants normally encountered penetrate the beds only slowly and that rarely do substances occur of a sufficiently high volatility to penetrate rapidly, for example a layer of charcoal 50 cm thick at a linear air velocity of 50 cm/s. Gas chromatography has proved a reliable analytical method for determining the chemical nature of filter poisons. A further simple design of removable charcoal sampler which allowed samples to be withdrawn directly from downward – or horizontal – flow deep-bed filters was described in /28/, fig. 8a and 8b. This has enabled useful ageing data /14/ to be obtained during in-service use. In-situ testing /28/ of plants fitted with this type of sampler has shown no leakage problems with this sampler design.

Since the ageing and poisoning of charcoal filters is a critical problem in iodine filtration today, iodine filter plants should on principle be fitted with apparatus for obtaining representative charcoal samples. The discussions showed that technology generally has not yet reached the stage where such features are readily available.

## Retention efficiency achievable with iodine filters

No agreement has as yet been reached as to the achievable retention efficiency of iodine filters. In the case of the deep-bed vessel-type filters, at least, there is considerable improvement in performance if the bed is made deeper, which can be done without great expense. Performance requirements, however, are still somewhat arbitrary, particularly as below certain limits there are no guidelines for the release of activity from power stations apart from a rather vague formulation : "as low as readily achievable". When the question arises as to the minimum removal efficiency below which an iodine filter should be changed, the usual practice will be to consult the licensing data. The latter do not necessarily correspond to the current state of technology. Enquiries among those present at the meeting showed that a minimum decontamination factor of 1,000 for radioactive iodine and radioactive methyl iodide was considered reasonable for iodine filters used to filter exhaust gases.

If iodine filters with shallow beds (or low stay times) are being used, a DF of 1,000 for methyl iodide under high humidity conditions cannot easily be achieved with sufficient certainty. The relatively low values quoted by the USAEC /17/ seem to reflect this situation.

In order to specify the required decontamination factor for an iodine filter plant, it is necessary to know the composition of the mixture of iodine compounds in the air as it flows through the filter. A few data on this point emerged from the discussion. In Germany, the currently accepted iodine composition in the reactor containment after a serious reactor accident is 85 % elemental iodine, 10 % methyl iodide, and 5 % particulate iodine, whereas in the USAEC Regulatory Guide, 1.52, the following values are laid down : 91 % elemental iodine, 4 % methyl iodide, and 5 % particulate iodine.

## Conclusions

Operating experience and the results of tests carried out on iodine filter units show that high efficiencies can be achieved if the filters are working correctly and impregnated charcoal is used.

A number of reports mentioned mechanical leakage in the filter

plants, yet it could clearly be seen from the papers presented that designs do exist in which virtually no leaks occur and which, when the necessary effort is made, eliminate /28/ /27/ /15/ or obviate the causes of leakage, such as imperfect weld seams, faulty valves in the by-pass, loss of charcoal caused by unsatisfactory supports, abrasion or settling of the charcoal.

Most of the papers showed that the problem of the ageing and poisoning of charcoal while it is being used in an iodine filter is fully recognized, but to a large extent unsolved, and there is therefore considerable uncertainty as to the retention efficiency that may be expected at any given time. Only in absence of poisoning effects deterioration may be predicted as mentioned by British authors /14/. It was reported that activated charcoal had been poisoned by aliphatic compounds /28/ /29/, oil and solvents, and that gas chromatography was used to determine the nature of the filter contaminants /15/. Many laboratory tests have been carried out on samples of the original charcoal from the iodine filters or on by-pass samples, but the results obtained have not been unequivocal enough for any firm estimates to be made as to the performance of the iodine filters over long periods in operation.

Iodine filters with deep charcoal beds, and therefore a longer residence time, have comparatively longer service lives, since the filter contaminants, provided they are not too volatile, have already been retained by the initial layers of activated charcoal. Complete separation of emergency filters and filters used during normal operation increases the level of safety, since in this case the iodine filter used to control the consequences of any accident would be largely free of any prior contamination.

The data provided on the behaviour of iodine filters should be taken as a starting point for essential work on the development of iodine sorption materials with improved resistance to ageing and poisoning and for research into the separation of poisons from the air flowing into the filters.

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## FINAL REMARKS

Although the statements in the preceding chapters are composed from different points of view, they endeavour to cover as fully as possible the problems of iodine filtration, which confront the designers of ventilation systems and filters on the one hand and the power station management and the licensing authorities or control organisations on the other hand.

The variable origin of the sorbent material, the physicochemical complexity of the sorption phenomenon, the very limited experience with sorbent materials on an industrial scale under extreme operational conditions, the lack of coordination with respect to quality control and sorption measurement techniques constitute the main reasons why in technical discussions concerning this subject different ways of presentation can be found and different standards applied.

The fact that during the seminar only very little information could be gathered about legal requirements and administrative rules to be followed in the field of iodine filtering, may be attributed to this situation, too. Pragmatic solutions and ad-hoc studies have been hitherto more common in this field than precise regulation.

USAEC Regulatory Guide 1.52 *) represents a step forward in the specification of design, operational conditions, maintenance and testing procedures for certain types of filter installation. It is likely that some of the principles laid down in this guide will also be followed in European countries, as long as no other recommendation is available.

The European Commission, being aware of this situation in the field of iodine filtration, has willingly taken up the suggestion raised during the seminar to organise an intercomparison of iodine sorbent test methods

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*) Regulatory Guide 1.52 "Design, testing, maintenance criteria for atmosphere clean-up system air filtration and adsorption units of light-water cooled nuclear power plants", USAEC June 1973, reproduced in /17/, see Seminar vol.I, pp. 555-563.

made on the same material by different laboratories *). It is expected that proceeding in this manner will be the best way to stimulate a coordination in filter testing and measurement techniques. It should be an objective that at least one laboratory in each Member State works according to the principles and methods developed within this series of intercomparison tests. Once this aim is achieved, it will be easier for the plant operators and the control organisations to obtain reliable information about the actual quality of the sorbent material which is in use.

This is not the place to present an appreciation of the improvements obtained in filter techniques. This has been done in detail above and es-pecially in Volume I of the Seminar Proceedings. In view of the importance which has to be attributed to iodine removal techniques in the frame of fu-ture energy programmes and in view of the desirable development in this field, it may be useful to emphasize here some important items mentioned in the body of this report, which urgently require solutions or at least more attention than they have found hitherto.

Such items comprise :

(a) for the attention of charcoal manufacturers and/or filter designers

- origin of poisoning and ageing of the sorbent material; abrasion and settling phenomena

- sorbent sampling from the bulk filter material

- leak-free design of filter plants

- optimisation of bed depth (deep versus shallow bed)

- radiation effects;

(b) for the attention of plant operators and/or test laboratories

- following up design and construction of filter plants (accessibi-lity for testing and maintenance purposes)

- ensure full information is provided on plant design, sorbent ma-terial behaviour under special operating conditions, the inter-

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*) The first test series are already running; a list of the laboratories that participate in this intercomparison programme is annexed (p. 76).

action of the sorption plant performance with other plant items
and factors such as inspection and maintenance (also of interest
to designers)

- processes of formation of penetrating species of iodine, the de-
tection of iodine compounds by means of advanced analytical proce-
dures;

(c) for the attention of licensing authorities and control organisations

- guidance and rules concerning design, operation, maintenance, and
testing of iodine sorbent systems, including continued in-situ
testing

- establishment of limits and admissible margins for retention effi-
ciencies in relation to practical experience, i.e. related to the
required and practicable DF.

It is hoped, that at another seminar or symposium about iodine filter
problems to be held in the future, say after a few years – as was repeated-
ly recommended by participants – more laboratories can report from their
experience and that more groups and authorities will then present their
opinion and comment.

\*            \*

\*

## ELEMENTS DE BASE *)

Paul Sigli

### INTRODUCTION

La première session de ce séminaire a été consacree aux principes de base régissant le piégeage de l'iode. Le problème posé en effet par ce produit de fission reste critique tout particulièrement dans le cas d'accident de réacteur; depuis déjà plus d'une dizaine d'années, les chercheurs de tous les pays utilisant l'énergie nucléaire se sont attachés à en limiter les rejets atmosphériques. Pour cela, des études sur le comportement physique ou chimique de l'iode élémentaire ou de ses composés ont amené à concevoir des pièges devant réduire sinon annuler tout rejet vers l'environnement. Des produits susceptibles de piéger aussi bien l'iode que les composés évoqués ci-dessus, dans des conditions variées, ont donc été développés à cet effet.

Les six communications de cette première session ont traité, en conséquence :

– d'une part, des propriétés générales des adsorbants vis-à-vis des différentes combinaisons de l'iode;

– d'autre part, des différentes formes d'iode pouvant se présenter au cours d'un accident, et de l'origine de ces formes;

– enfin, du vieillissement des adsorbants, problème important puisque c'est lui qui conditionne toute la politique à mener afin que le piège soit réellement efficace le jour où un rejet gazeux vers l'atmosphère est envisagé.

Dans cet exposé, qui est une synthèse des travaux de la première session, nous reprendrons chacun des points ci-dessus. L'idée maîtresse développée par les différents auteurs ayant été mise en évidence, nous nous sommes attachés à extraire des discussions les points essentiels qui ont été soulevés par les participants, éventuellement en les précisant, afin d'essayer de faire apparaître les recherches qui semblent encore nécessaires pour combler les lacunes éventuelles. Toutefois, en ce qui concerne les propriétés

*) Bibliographie voir p.73 ; version anglaise voir p.3

générales des adsorbants, nous nous sommes volontairement bornés à un rappel succinct et on peut trouver de plus amples détails dans l'article ayant ouvert le séminaire /1/.

## 1. LES CONDITIONS DU PIEGEAGE DE L'IODE

La première étape vers la réalisation d'un piégeage des formes gazeuses de l'iode est le choix de l'adsorbant à utiliser; elle comprendra, de plus, l'étude de son comportement vis-à-vis des différentes formes physico-chimiques envisagées.

### 1.1. Les matériaux d'adsorption

L'adsorbant qui a été le plus étudié ces dernières années est certainement le charbon actif *). Il présente généralement de bonnes qualités de rétention vis-à-vis de l'iode moléculaire, mais il peut être aisément pénétré par l'iodure de méthyle surtout si l'hygrométrie relative est élevée. On peut, par exemple, s'en rendre compte sur la figure 1 (page 5 du volume I) présentée par J.G. WILHELM.**)On a remédié à cet inconvénient des charbons actifs en les imprégnant soit avec la triéthylènediamine (TEDA) généralement à 5 %, soit avec de l'iodure de potassium ou même de l'iode élémentaire (ou en mélange des deux) dans des proportions variant de 0,5 à quelques pourcent.

La granulométrie du support de charbon utilisé influence très largement le résultat final. Si la taille des grains diminue, l'efficacité augmente. Toutefois la perte de charge qui augmente également avec la diminution de la taille des grains sera un facteur limitatif dans cette voie. Pratiquement, la granulométrie utilisée est telle que les diamètres des grains sont compris entre 1 et 4 mm; toutefois dans le cas des matériaux extrudés, la longueur peut être plus grande.

Ces adsorbants présentaient cependant l'inconvénient d'être empoisonnés par les oxydes d'azote ($NO_2$ notamment) et de ne pouvoir fonctionner

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*) Dans le présent contexte, il est entendu que nous utiliserons indifféremment charbon actif ou charbon avec la même signification.

**) Version anglaise voir p. 77 de ce volume.

qu'à des températures relativement basses. C'est ainsi que des matériaux imprégnés à l'argent furent développés, comme les tamis moléculaires ou le produit AC 6120 /1/ *), dont les qualités les rendaient aptes à travailler dans des conditions où les charbons ne pouvaient plus être utilisés. C'est tout particulièrement le cas de l'utilisation d'un adsorbant solide pour les usines de retraitement de combustible, où l'utilisation des charbons est à proscrire à cause des oxydes d'azote, d'une part, et des risques d'incendie, voire d'explosion, d'autre part.

## 1.2. Influence de l'humidité du gaz porteur sur l'efficacité

L'adsorption de l'iode élémentaire et de l'iodure de méthyle est diminuée si la surface active de l'adsorbant a fixé de l'eau. Ce phénomène est tout particulièrement sensible pour l'iodure de méthyle.

A une humidité relative située en dessous de 30 à 40 %, on note peu d'effet sur l'efficacité, mais quand l'hygrométrie augmente, le pouvoir de rétention chute, surtout au-dessus de 70 %. Des produits ont cependant été développés qui permettent une utilisation à près de 100 % d'hygrométrie.

## 1.3. Adsorption à température élevée

L'élévation de température - rendue parfois nécessaire si l'hygrométrie relative est élevée - peut se traduire sur le charbon actif imprégné par les paramètres suivants /1/ :
   - perte d'imprégnant, donc détérioration des qualités du lit adsorbant,
   - désorption des produits fixés au préalable,
   - inflammation du lit d'adsorbant.

La limite supérieure pratique d'utilisation d'un charbon imprégné dans l'air se situera donc généralement en dessous de 100°C. Si la filtration exigeait une température supérieure, il faudrait recourir aux adsorbants minéraux dont nous avons parlé précédemment.

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*) Fabriqué sur la base d'acide silicique amorphe spécialement conditionné et imprégné avec du nitrate d'argent.

## 1.4. Influence de la concentration en iode du gaz porteur

Les concentrations en iode dans le débit d'air de ventilation d'un réacteur en fonctionnement normal, atteignent des valeurs très faibles, par exemple $10^{-4}$ à $10^{-6} \mu g.m^{-3}$. Le problème se pose donc de savoir comment se comporte l'efficacité des adsorbants lorsque la concentration en iode dans le gaz porteur atteint des valeurs aussi faibles.

Une première constatation est que, pour les très basses concentrations, il y a chute d'efficacité. WILHELM /1/ précise qu'il n'est pas possible de donner une valeur fixe inférieure à partir de laquelle cet abaissement se produit. Un tel abaissement a été signalé aussi bien pour les charbons activés que pour les zéolithes /2/.

Les travaux allemands montrent par ailleurs qu'il existe une différence de comportement des pièges suivant que la concentration en $ICH_3$ est réalisée par dilution dans de l'air ou par préfiltration. Dans le premier cas, le comportement aux faibles ou aux grandes concentrations est identique sur une plage représentant un facteur $10^9$, tandis que, dans le deuxième cas, l'abaissement de l'efficacité après préfiltration a lieu aussi bien pour les faibles concentrations que pour les concentrations plus élevées. Ceci suggère qu'on étudie peut-être non seulement l'influence de la concentration, mais également l'influence d'une forme nouvelle et plus pénétrante que celle qu'on veut tester. Nous réexaminerons plus en détail cette question au paragraphe 2.1.

## 2. LES FORMES PHYSICO-CHIMIQUES DE L'IODE PRESENTES DANS UN REACTEUR

## 2.1. Mise en évidence de l'iodure de méthyle et des formes pénétrantes

A la suite d'expériences entreprises en Grande-Bretagne, MEGAW et MAY /3/ montrèrent que l'iode élémentaire introduit dans l'enceinte du réacteur Pluto disparaissait rapidement tandis que la fraction restante semblait beaucoup plus difficile à piéger. Une identification de cette fraction difficilement adsorbable fut alors entreprise par EGGLETON et ATKINS /4/ /5/.

L'iode était généré à partir d'iodure de sodium, passé sur "knit-mesh" de cuivre puis filtré, et la partie considérée comme pénétrante condensée dans un piège froid. Tandis qu'une fraction, soluble dans le benzène et l'eau, restait non identifiée, la seconde partie était identifiée comme étant des iodures d'alkyles, les deux constituants majeurs étant l'iodure de méthyle (85 %) et l'iodure d'éthyle (3 %). Ces travaux, qui mettaient en évidence pour la première fois les formes pénétrantes de l'iode, furent d'une importance capitale puisqu'ils allaient orienter et influencer les recherches de ces dix dernières années. On peut dire sans grand risque que les travaux ultérieurs ne remirent pas en cause cette identification, mais plutôt qu'ils confirmèrent que l'iodure de méthyle avait effectivement le comportement d'une forme pénétrante.

Au fur et à mesure que les travaux se poursuivaient sur le comportement des pièges vis-à-vis de l'iodure de méthyle, il apparut qu'une forme au moins s'avérait encore plus pénétrante que l'iodure de méthyle (voir par exemple la figure 5, page 12 de la référence /1/). A la 10th Air Cleaning Conference, F.O. CARTAN, H.R. BEARD, F.A. DUCE, J.H. KELLER /6/ insistèrent sur le fait qu'une forme pénétrante non organique était piégée sur l'oxyde de zirconium hydraté chargé à l'iode. Cette forme, suivant les auteurs, pourrait être l'acide hypoiodeux HOI. La principale objection faite à cette hypothèse fut que l'acide hypoiodeux était instable d'une part, et peu volatil d'autre part. La 11th Air Cleaning Conference apporta, de la part de ces mêmes auteurs /2/, une tentative d'identification du composé incriminé. Mais il n'en reste pas moins vrai que l'hypothèse de l'existence de l'acide hypoiodeux comme forme pénétrante ne se trouve justifiée que par des preuves indirectes, et qu'une identification ultérieure reste toujours à réaliser.

Au cours du séminaire de Karlsruhe, WILHELM émit l'idée que l'acide iodique $IO_3H$ pourrait avoir également une tension de vapeur suffisante pour qu'on puisse le retrouver dans la phase gazeuse, et conduire ainsi à une forme inorganique difficile à arrêter. Toutefois, les travaux allemands ne permettent pas, dans l'état actuel des choses, de conclure de manière définitive.

Durant les discussions, il était indiqué que les recherches entre-
prises au niveau du piégeage des faibles concentrations d'iodure de méthyle,
tendent à prouver que les pénétrations plus élevées, observées dans ces
conditions, ne sont pas nécessairement dues au seul effet de concentration
mais pourraient bien provenir de la présence d'une forme très pénétrante.
Cette forme ne serait mise en évidence que lorsque l'efficacité des adsor-
bants utilisés a diminué l'activité en iodure de méthyle de quelques ordres
de grandeur, pour que l'activité d'une "impureté" devienne prépondérante.
En fait, toute la difficulté d'une telle étude, aux très faibles concentra-
tions d'iode, apparaît clairement si on se souvient que l'air dans lequel
nous vivons contient une quantité de l'ordre du milligramme par mètre
cube en méthane, et une quantité d'iode de l'ordre de $10^{-3} \mu g\, m^{-3}$. La
grande réactivité de l'iode fait que, au cours d'une génération d'iodure
de méthyle, nous pourrons très bien produire une impureté, réaliste ou
non du cas réel dans un réacteur, qui risque parfois de fausser considéra-
blement le résultat de l'expérience du laboratoire.


## 2.2. Les formes physiques de l'iode

Dans tout ce qui précède, nous avons plus ou moins implicitement
admis que nous nous intéressions à la phase strictement gazeuse. La commu-
nication présentée par K. PFEIFFER /7/ montre qu'il faut prendre en compte
également des formes aérosols et l'auteur donne la composition de l'activi-
té qu'il a pu mettre en évidence sur le réacteur du BWR de Gundremmingen.
Grâce à un échantillonneur composé :
- de filtres en fibres d'amiante,
- de cartouches de charbon actif,
- de cartouches de charbon actif imprégné à 1 % d'iodure de potassium
- et de cartouches d'AC 6120 imprégné à l'argent,
qu'il dispose en ordres variés, l'auteur arrive à la conclusion que la
répartition d'activité s'effectue de la manière suivante (au niveau de la
ventilation) :
- aérosols : 40 %
- éléments facilement piégés par le charbon actif : 50 %
- formes pénétrantes : 7 %
PFEIFFER note également que cette composition est grandement variable

suivant le point d'échantillonnage.

On peut trouver plusieurs origines à cette quantité importante d'iode sous forme d'aérosol. Il peut s'agir d'aérosols liquides ou solides dans lesquels l'iode peut être ou partie intégrante de l'aérosol, ou seulement fixé par adsorption. En tout état de cause, l'auteur note que ces aérosols sont mal retenus sur le charbon actif. Deux expériences menées en parallèle montrent en effet que le filtre du premier pack, placé en aval des cartouches de charbon, donne une activité similaire à celle prélevée sur le filtre, disposé en amont, dans le deuxième pack. Cette expérience prouve de plus que les aérosols ne sont pas formés sur le charbon (adsorption sur des poussières de charbon actif par exemple).


## 2.3. Origine de l'iode

Dans la communication de J. BARBIER /8/, on trouve l'idée que l'iode-131 rejeté par un réacteur dans l'atmosphère pourrait provenir de son précurseur le tellure-131, non arrêté ni par les filtres haute efficacité, ni par le piège à charbon actif.

Des expériences menées en Grande-Bretagne /9/ ont cependant montré que des échantillons de combustible irradié et chauffé dans du gaz carbonique de manière à fondre le gainage d'acier inoxydable et une partie du combustible lui-même, laisseraient échapper des produits de fission $^{132}Te$, $^{137}Cs$ ou $^{90}Sr$, sous forme particulaire qui, dès lors, pouvaient être aisément arrêtés sur les filtres (HEPA).

D'autre part, il était avancé au cours des discussions qu'il n'y aurait pas une quantité suffisante de tellure volatilisé pour expliquer les fortes teneurs en iode trouvées dans les rejets. Ceci donne un support à l'idée que l'iode présent dans le fluide caloporteur - gaz ou liquide - ne doit pas être grandement influencé par ses ascendants.

L'importance de la présence du tellure dans le circuit de refroidissement ne semble pas encore définitivement démontrée, mais une série d'expériences susceptibles de faire la lumière sur ce point précis pourrait être envisagée.

## 2.4. Origine de l'iodure de méthyle

Deux conférences /10/ /12/ avaient trait au comportement de l'iode dans un réacteur. La première communication de J.J. HILLARY /10/ fait état du comportement d'iode-131 de fission relâché dans le fluide caloporteur d'un réacteur AGR à partir d'éléments de combustible défectueux et, par ailleurs, du comportement d'iodure de méthyle délibérément introduit dans le réacteur. Dans le premier cas, l'iode a été trouvé se présenter principalement sous forme d'iodure de méthyle, tandis que 10 % se trouvaient sous forme aérosol ou iode élémentaire. Toutefois, l'auteur note qu'il est sans doute probable qu'une partie de l'iode particulaire ou de l'iode moléculaire ait pu être fixée sur les tuyauteries d'échantillonnage, ce qui risque de fausser le bilan final. Finalement, le rapport du contenu en iode relâché du combustible, à la quantité d'iode trouvée présent dans le gaz (après décomposition/déposition) était de 4 500, ce qui représente le facteur de décontamination de l'ensemble de l'installation. L'iodure de méthyle introduit délibérément dans le circuit de refroidissement du réacteur montre un comportement qualitativement analogue à celui de l'iode de fission puisque sa vitesse de disparition est grande au moins initialement.

L'expérience réalisée en France /12/ sur le réacteur graphite-gaz de Chinon I consistait en l'injection d'iode élémentaire dans le circuit de refroidissement. Les conclusions essentielles furent les suivantes :

- l'iode est trouvé dès les premiers instants de mesure sous forme pénétrante;
- la concentration de cette forme pénétrante décroît rapidement dans le temps.

On peut noter que ces deux communications concourent en fait à une conclusion similaire : prépondérance des formes pénétrantes dans la phase gazeuse et piégeage de ces formes par les structures du réacteur.

Finalement, ce qui intéresse le scientifique chargé de prévoir ce qui peut se passer dans un cas accidentel, c'est justement la composition de la phase gazeuse, et les espèces qui peuvent s'y rencontrer, afin de déterminer sa conduite de rejet vers l'atmosphère. En fait, il semble bien qu'on doive admettre que l'iodure de méthyle ne trouve pas sa source dans

le combustible lui-même, pas plus qu'en phase liquide (cas des LWR), mais
bien en phase gazeuse. Une étude critique réalisée par POSTMA et
ZAVADOVSKY /13/ sur les origines possibles de l'iodure de méthyle conclut
que l'origine la plus plausible est une formation radiolytique, en phase
gazeuse. Comme on l'a vu plus haut, l'air contient des impuretés organiques
en quantité non négligeable. L'air du confinement d'un réacteur à eau
légère sera encore plus chargé de vapeurs organiques de toutes provenances,
et, dans le cas accidentel, soumis en permanence à des doses de rayonnement
élevé donnant, à tout moment des radicaux libres, essentiellement $CH_3$, ce
qui tout naturellement conduit à la formation d'iodure de méthyle. Finale-
ment, les auteurs américains concluent que l'iodure de méthyle, dans un cas
précis et pour un intervalle de temps donné, doit représenter quelque
chose comme 3 % de l'iode présent dans la phase gazeuse, cet iode ne
représentant lui-même que 25 % de l'inventaire total du coeur.

Il faut bien comprendre que ces derniers chiffres, beaucoup plus bas
que ceux avancés précédemment, ne sont pas nécessairement incompatibles.
Les pourcentages élevés d'iodure de méthyle observés en fonctionnement
normal d'un réacteur graphite-gaz pourraient alors s'interpréter comme
résultant d'un enrichissement dû à la disparition de la forme élémentaire
sur les surfaces du réacteur. Un phénomène analogue doit se faire jour sur
n'importe quel réacteur, la proportion en iodure de méthyle devant augmen-
ter avec la distance au point où l'iode a été émis.

Un autre point d'intérêt est de connaître finalement la forme sous
laquelle l'iode va se trouver au point de rejet. Il est certain que, la
proportion relative d'iodure de méthyle augmentant, le risque de contamina-
tion de la chaîne alimentaire herbe-bétail-lait, diminue d'autant.

La connaissance de l'origine de la formation d'iodure de méthyle et
de sa proportion probable dans un rejet atmosphérique conduit à une approche
plus précise du risque résultant d'une émission accidentelle d'iode.
Bien que de nombreuses études aient été effectuées dans ce sens, il semble
bien qu'il faille encore préciser le comportement de l'iode (ou de ses
composés) depuis sa formation jusqu'à ce rejet atmosphérique.

## 2.5. Evaluation d'accidents de réacteur

Une communication de J.J. HILLARY /11/ reproduit en laboratoire des conditions accidentelles dans un SGHWR. La libération de produits de fission est réalisée à partir de combustibles rendus artificiellement défectueux par chauffage à 1 000°C dans un courant de vapeur et d'argon. Les auteurs arrivent à la conclusion que le taux d'émission de $^{133}$Xe et de $^{131}$I dépend des conditions d'irradiation. Finalement, ils proposent une série de facteurs pour prédire la libération d'iode total ou d'iode sous forme pénétrante à partir de l'activité mesurée des gaz rares. On rappelle ci-dessous ces facteurs :

Facteurs pour déterminer
la libération

|  | d'iode total | des formes pénétrantes |
|---|---|---|
| $\dfrac{\text{Xe-133}}{\text{I-131}}$ | 7 | 70 |
| $\dfrac{\text{Kr-85}}{\text{I-131}}$ | 70 | 700 |

Le taux de combustion joue un rôle sur la quantité totale d'iode considérée comme stable ($^{127}$I + $^{129}$I) formé. Il a été suggéré qu'il se formerait d'autant moins d'iodure de méthyle que la quantité d'iode globale était plus grande. Mais en fait, ne s'agit-il pas plutôt de la proportion relative impuretés organiques-iode qui finalement régirait la réaction et conduirait à la quantité finale de formes pénétrantes?

Au cours de ce chapitre traitant des formes physico-chimiques de l'iode, nous avons pu constater que ce point semblait toujours le point essentiel. L'origine de l'iodure de méthyle, ou la nature même des formes dites pénétrantes d'iode, restent à établir de manière définitive.

## 3. LE VIEILLISSEMENT DES CHARBONS IMPREGNES

### 3.1. Comment le vieillissement affecte-t-il les pièges?

Un problème des plus sérieux est posé par l'altération des propriétés de rétention des charbons vis-à-vis de l'iode ou de l'iodure de méthyle, en fonction du temps. C'est ce phénomène, assez mal connu, qui fait qu'un piège en service, soit de manière continue, soit de façon intermittente,

possède à un moment déterminé une efficacité inférieure à celle mesurée au
départ. En tout état de cause, l'exploitant d'une installation désire
connaître ce à quoi il peut s'attendre comme valeur de rétention des
différentes formes d'iode. C'est pourquoi on est amené à effectuer des
contrôles périodiques sur les pièges mêmes de l'installation toute entière.
L'importance de ces phénomènes de vieillissement et du contrôle in situ des
pièges est telle qu'elle a justifié le titre même de notre séminaire.

La contribution de L.R. TAYLOR et R. TAYLOR /14/ portait précisément
sur l'étude de ce vieillissement. Les travaux anglais menés depuis quelques
années sur ce sujet tentent de simuler l'évolution de l'efficacité d'un
support de charbon imprégné soit à l'iodure de potassium soit à la
triéthylènediamine, à la fois de manière dynamique et de manière statique.

Un indice de vieillissement est utilisé pour exprimer ce vieillisse-
ment dynamique; c'est le nombre de fois qu'un volume d'air égal au volume
du lit de charbon a été passé sur le piège. C'est ce que nous appellerons
plus commodément le nombre de renouvellements.

On peut, dans le cas de l'iodure de méthyle, définir un indice de
performance K égal au $\log_{10}$ de l'efficacité E divisé par le temps de
séjour t :

$$K = \frac{\log_{10} E}{t}$$

dans lequel :

$$t = \frac{\text{volume du lit de charbon}}{\text{débit}}$$

L'auteur arrive à la conclusion que cet indice de performance peut
être exprimé en fonction du nombre de renouvellements subis par le piège,
par une loi du type :

$$\log_{10} K = \log_{10} K_0 - C_1 N$$

où $K_0$ est l'indice de performance initial du piège

$C_1$ une constante

N le nombre de renouvellement depuis l'instant initial.

De la même manière, cet indice de performance serait lié à l'âge de l'adsorbant par une loi linéaire de la forme :

$$\log_{10}K = \log_{10}K_0 - C_2\,\tau$$

où $\tau$ est l'âge du charbon en semaines

$C_2$ une constante.

Les constantes, pour ces deux équations, ont été déterminées (pour un charbon donné utilisé dans l'air) à la fois en laboratoire et dans des conditions réelles d'exploitation dans des conditions dynamiques et statiques. Dans ce cas :

$$\log_{10}K = \log_{10}K_0 - 0,3.10^{-8}N - 1,3.10^{-3}\tau$$

## 3.2. Discussion autour du vieillissement

Une des premières questions qui vient à l'esprit est de se demander à quoi est dû ce vieillissement ? Si en effet la loi proposée rend compte de l'évolution du phénomène avec le temps, elle en ignore en fait les causes. Lorsqu'on considère un charbon imprégné dans son emballage d'origine qui en principe le maintient à l'abri de l'air, on observe malgré tout un vieillissement. Des exemples peuvent être trouvés /15/ dans lesquels le charbon a été rendu impropre à la filtration plus rapidement que ne laissait entrevoir la relation ci-dessus. Il a été suggéré /14/ que ce vieillissement pourrait provenir d'une substance contenue dans la base du charbon elle-même et le soufre est suspecté comme agent possible du vieillissement. Une autre cause pourrait être la recristallisation de l'imprégnant. Le vieillissement dynamique d'un charbon pourrait faire également penser à une oxydation lente, due à l'oxygène de l'air.

Il semble bien toutefois qu'il faille distinguer vieillissement et empoisonnement si l'on veut pouvoir appliquer les équations évoquées plus haut. Ces équations ne peuvent rendre compte du vieillissement qu'à la condition que la composition de l'air circulant sur le piège ait une composition standard et qu'aucun contaminant majeur des pièges – huile, vapeurs de solvants, etc. – n'intervienne, sinon le mot de vieillissement peut être mal interprété s'il n'est pas convenablement défini.

Si l'on tentait de résumer la situation, nous pourrions dire, sachant que le piège nécessairement vieillira et que de plus il risque d'être soumis à des "poisons", qu'il est préférable de largement dimensionner les pièges de manière à ce que ceux-ci montrent initialement une performance très supérieure au minimum requis par le cahier des charges. La limitation sera évidemment constituée par le coût final de l'opération, mais en aucun cas il n'est recommandable de se satisfaire des performances minimales.

CONCLUSION

En guise de conclusion aux réflexions des participants, réflexions qui ont constitué la base des développements de cet article, il serait bons, croyons-nous, d'insister sur les points essentiels, qui, tout au long de cette session, nous ont semblé mal éclaircis, et qui pourraient mériter à l'avenir des études complémentaires.

1° Caractérisation définitive des formes pénétrantes d'iode (IOH, $IO_3H$) mettant en jeu des processus analytiques élaborés – spectrométrie de masse – par exemple.

2° Mécanismes de formation de ces formes pénétrantes. Il a été montré qu'un mécanisme possible de formation de l'iodure de méthyle – pour se borner à ce seul composé – serait une réaction radiolytique en phase gazeuse. De nouveaux travaux en laboratoire, dans des conditions réalistes pouvant se rencontrer en réacteur, pourraient sans doute infirmer ou confirmer cette hypothèse et pourquoi pas, quantifier de manière plus précise la composition du gaz à épurer.

3° Quant au problème du vieillissement des adsorbants, les études sont évidemment très longues. Mais ne pourrait-on pas, dans un proche avenir, essayer de collationner l'ensemble des résultats obtenus lors de tests in situ par exemple et tenter d'exploiter si cela est réaliste, les données ainsi obtenues en se référant par exemple à l'indice de performance proposé dans les travaux anglais ?

Un premier pas dans ce sens a été réalisé à Karlsruhe par la mise sur pied d'une confrontation des techniques utilisées dans les différents

laboratoires, qui sera suivie d'une comparaison entre les différents matériaux d'adsorption.

Les Communautés Européennes ont proposé une nouvelle réunion dans quelques années sur le thème des "pièges à iode". Peut-être y verrons-nous surgir les éléments nouveaux qui nous manquent à l'heure actuelle ? C'est pour notre part le voeu que nous formulons.

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PRUEFMETHODEN UND BETRIEBSERFAHRUNGEN *)

J. G. Wilhelm

## Einleitung

Prüfungen von Jod-Sorptionsmaterialien im Labor und von Jodfiltern im
eingebauten Zustand gehören zu den üblichen Ueberwachungsaufgaben,
die die Verfügbarkeit und zuverlässige Leistung einer sicherheits-
technisch bedeutenden Komponente der Kerntechnik zu gewährleisten ha-
ben. Derartige Prüfungen werden in praktisch allen Ländern durchge-
führt, die über entsprechend ausgerüstete kerntechnische Anlagen ver-
fügen. Die Uebertragbarkeit der Prüfergebnisse ist dadurch begrenzt,
dass die angewandten Verfahren und Prüfbedingungen nicht ausreichend
detailliert bekannt sind und eine internationale Festlegung bisher
nicht angestrebt wurde. Dies ist nicht nur eine Erschwernis für den
Hersteller, der Jodfilter auf einem internationalen Markt verkaufen
will, sowie für den Käufer und den Gutachter, der die Funktionstüch-
tigkeit von Jodfiltern zu akzeptieren bzw. zu begutachten hat. Es ist
auch ein Problem für den Prüfer, der die im eigenen Labor gemessenen
Werte nicht ohne weiteres mit fremden Daten vergleichen kann und da-
durch einer gewissen Unsicherheit in bezug auf die Gültigkeit seiner
Ergebnisse ausgesetzt ist. Das Seminar über Jodfilter und ihre Prü-
fung bot Gelegenheit, durch Vorträge und intensive Diskussion zwischen
den Beteiligten einschlägige Prüfverfahren im Detail zu erörtern und
eine gemeinsame Basis für Vergleichsmessungen zu finden.

## Prüfmittel zur Messung der Durchlässigkeit von Jod-Sorptionsmate-
rialien und Jodfiltern

Uebereinstimmend wurde in sämtlichen Referaten, die von Autoren aus
Deutschland /36/, England /37/, Frankreich /38/, Italien /39/, den
Niederlanden /40/ und Schweden /35/ vorgetragen wurden, mit $^{131}$J mar-
kiertes Methyljodid (Gemisch von $CH_3^{131}J + CH_3^{127}J$) als geeignetes
Prüfmittel sowohl für Laborprüfungen des Jod-Sorptionsmaterials als
auch für Vor Ort-Prüfungen von Jodfiltern bezeichnet und über

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*) Bibliographie siehe S. 73 ; englische Uebersetzung siehe S. 29

entsprechende Versuchstechniken zu seinem Einsatz berichtet. In einigen Referaten würde ausserdem auf die Verwendung von radioaktiv markiertem elementarem Jod hingewiesen. Eine Gegenüberstellung der Eigenschaften dieser beiden Prüfmittel, die in mehreren Vorträgen, zum Beispiel /37/, durchgeführt wurde, zeigte, dass Methyljodid bei der Vor Ort-Prüfung wegen seiner einfacheren Herstellungsmethode, leichteren Handhabung, höheren Flüchtigkeit und relativ grossen Reaktionsträgheit im Verhältnis zu elementarem Jod wesentliche Vorteile aufweist. Der Einsatz von elementarem, radioaktiv markiertem Jod als Prüfmittel anstelle von Methyljodid ist gewöhnlich nur dann bei der Vor Ort-Prüfung nicht zu umgehen, wenn es sich um die Prüfung der Leckdichtigkeit von Jodfiltern handelt, die mit einer Aktivkohle ohne Imprägnierung ausgestattet sind. Derartige Filter, die eine Abscheidung organischer Jodverbindungen nur unzureichend gewährleisten, sollten in kerntechnischen Anlagen nicht verwendet werden. Die Adsorption von elementarem Jod an Oberflächen, die u.a. die Durchführung von Vor Ort-Prüfungen sehr erschwert, kann, wie berichtet wurde /38/ /32/, durch eine vor der Vor Ort-Prüfung durchzuführende Absättigung mit inaktivem elementarem Jod reduziert werden.

Grosses Interesse, das sich in entsprechenden Diskussionen ausdrückte, bestand in einem Vergleich zwischen der Vor Ort-Prüfung mit Methyljodid und dem in USA eingeführten Prüfverfahren unter Benutzung von Freonen /41/. Freone erfordern als inaktives Prüfmittel keine strahlenschutztechnischen Vorsichtsmassnahmen. Trotzdem haben sich Freon-Prüfverfahren in Europa nicht durchgesetzt, nur zwei Vorträge /39/ /30/, enthielten Angaben zum Freon-Prüfverfahren und der dazu notwendigen Instrumentierung. Der experimentelle Aufwand, der durch notwendige Vorversuche zur quantitativen Messung kleinster Freonkonzentrationen mittels gas-chromatographischer Methoden verursacht wird, scheint unverhältnismässig grösser zu sein als bei Anwendung der $CH_3^{131}J$-Prüfmethode. Bei dieser wird zur Auswertung nur ein Messplatz vorausgesetzt, der im Rahmen der üblichen Grundausstattung eines Strahlenschutzlabors in kerntechnischen Anlagen erwartet werden kann.

In der lebhaften Diskussion zur Anwendbarkeit des $CH_3^{131}J$- und des Freon-Prüfverfahrens wurden folgende Punkte aufgegriffen:

1. Vergleich des Zeitbedarfs zur Durchführung der Filterprüfung.

   Der Zeitaufwand zur Feststellung eines Lecks dürfte sich bei
   beiden Methoden in etwa entsprechen, wenn man die Zeit zur
   Herstellung des radioaktiv markierten Methyljodids nicht ein-
   rechnet.

2. Möglichkeit der Beseitigung von Lecks unmittelbar nach ihrer
   Feststellung bei der Vor Ort-Prüfung.

   Bei Anwendung von Filterwänden, die mit Aktivkohlefilterzellen
   bestückt sind, könnten sich bei Anwendung von Freon als Prüfmit-
   tel Vorteile ergeben, da keine radioaktive Kontamination der Fil-
   ter durch das Prüfmittel erfolgt. Bei Prüfung von Jodfilteranla-
   gen, die mit Filtergehäusen oder Filterbänken ausgestattet sind
   und die Anwendung der Sackwechseltechnik zulassen, sowie bei
   Schüttbettfiltern mit Beschickung der Aktivkohle durch Einfüll-
   öffnungen ausserhalb des kontaminierten Bereichs, ist die Konta-
   mination der Filter durch die Vor Ort-Prüfung jedoch von geringer
   Bedeutung. Bei Filtern, die ohnehin während der Betriebszeit kon-
   taminiert wurden, dürfte die zusätzliche Kontamination durch die
   Prüfung mit $CH_3^{131}J$ praktisch bedeutungslos sein.

Aus dem während des Seminars vorgelegten Material ist ein Vergleich
der Prüfergebnisse bei Anwendung von Freonen und $CH_3^{131}J$ in der Vor
Ort-Prüfung nicht in ausreichendem Maße möglich. Auch durch die Dis-
kussion ergab sich keine Klarheit. Selbst unter der Voraussetzung,
daß die Freon-Prüfung ausschließlich ein Lecktest zur Erkennung me-
chanischer Lecks ist und nicht, wie bei der Durchführung einer
$CH_3^{131}J$-Prüfung, Aussagen zur Rückhaltung von Spaltjod in der Aktiv-
kohle erlaubt, besteht berechtigtes Interesse an einem Vergleich der
Prüfergebnisse beider Verfahren, zumal die Freon-Prüfung in den USA
ein von der USAEC anerkanntes Prüfverfahren ist /17/. Zusätzliche Ar-
beit auf diesem Gebiet erscheint unbedingt notwendig, dies gilt eben-
falls in Hinsicht auf eventuelle Vergiftungseffekte, die durch Freon
in der Aktivkohle hervorgerufen werden könnten.

## Vor Ort-Prüfung von Jodfiltern mit radioaktiv markiertem Methyljodid

Die Vorträge zeigten, daß in den verschiedenen Ländern bei der Anwendung der Vor Ort-Prüfmethode unter Benutzung von $CH_3{}^{131}J$ nur geringe Unterschiede bestehen, die in dem Verfahren zur Prüfmittelherstellung, der Anzahl und Ausstattung der Roh- und Reinluft-Probensammler und verschiedenen Sammelzeiten während der Prüfung zum Ausdruck kommen. Uebereinstimmend wurde vom dem Einsatz von Prüfmittelaktivitäten zwischen 1 und 100 mCi $CH_3{}^{131}J$ berichtet; die im Einzelfall benötigte Aktivität wird durch den Volumenstrom durch das Filtersystem unter Test, den zur Aktivitätmessung entnommenen Teilstrom und die Nachweisgrenze der Messanordnung bestimmt. Wichtig erscheint, daß das Risiko einer nennenswerten Freisetzung von radioaktivem Prüfmittel durch Vorprüfung mit geringer Aktivität ausgeschaltet wird.

Diskutiert wurde, ob zur Probenahme während der Vor Ort-Prüfung die gleiche Aktivkohle wie im überprüften Jodfilter benutzt werden sollte oder ob man besser für die Ausstattung der Probensammler Aktivkohlen extrem hoher Abscheideleistung (z.B. mit sehr kleinen, in Jodfiltern nicht einsetzbaren Korngrößen) verwendet. Die Benutzung von Aktivkohle aus der Orginalcharge im Probensammler ermöglicht einen unmittelbaren Vergleich der Abscheideleistung zwischen der ungebrauchten Aktivkohle (bei Verwendung eines mehrstufigen Probensammlers) und der im Jodfilter durch den Betrieb gealterten und gegebenenfalls vergifteten Aktivkohle. Diesem Vorteil steht aber gegenüber, daß der Volumenstrom durch den Probensammler entsprechend der linearen Luftgeschwindigkeit im Jodfilter eingeschränkt werden muß. Das bereits ungünstige Verhältnis zwischen Volumenstrom durch das Jodfilter, der gewöhnlich mehrere 1000 bzw. 10000 $m^3/h$ beträgt und dem Teilstrom durch die Probensammler, der im Bereich zwischen ca. 0,1 und 10 $m^3/h$ liegt, wird dadurch noch größer. Außerdem ist diese Prüfmethode des Sorptionsmaterials ungenauer als eine Laborprüfung.

Auch die Ergebnisse von Vor Ort-Prüfungen mit radioaktiv markiertem Methyljodid können Anlaß zu Interpretationsschwierigkeiten geben. Eine Unsicherheit, auf die in der Diskussion hingewiesen wurde, besteht in der offensichtlich unvermeidbaren geringfügigen Verunreinigung des Prüfmittels mit noch stärker penetrierenden Jodverbindungen als Methyljodid. Bei der Prüfung von Tiefbett-Filtern mit extrem hohem Abschei-

degrad zeigte die reinluftseitig vom Jodfilter im Aktivkohle-Proben-
sammler abgeschiedene Aktivität häufig kein normales, durch eine Ex-
ponentialfunktion zu beschreibendes Abscheidungsprofil, sondern eine
unregelmäßige Verteilung, die nicht dem Abscheidungsverhalten von ele-
mentarem Jod bzw. Methyljodid entsprach und auf stark penetrierende
Jodverbindungen hinwies. Das Prüfergebnis ist in solchen Fällen nicht
nur durch die Summe aus mechanischem Leck und Durchlässigkeit gegen-
über dem elementaren Jod bzw. Methyljodid, sondern auch durch den An-
teil an stark penetrierenden Jodverbindungen im Prüfmittel bestimmt.
Durch eine sorgfältige Prüfung des Abscheidungsprofils der Prüfmittel-
aktivität in mehrstufigen Reinluft-Probensammlern können Fehlinter-
pretationen des Prüfergebnisses weitgehend ausgeschlossen werden. Bei
Verwendung von elementarem Jod als Prüfmittel wurde von den Autoren
eines Vortrages /33/ ein Verhältnis zwischen elementarem Jod und an-
deren Jodverbindungen in der Abluft festgestellt, das zwischen 1 : 15
und 1 : 670 schwankte; ein arithmetischer Mittelwert von 125 wurde
errechnet. Bei Anwendung von Methyljodid betrug das Verhältnis von
Methyljodid zu anderen Jodverbindungen 1 : 2 · $10^{-4}$ bis 1 : 0,1.

In diesem Zusammenhang waren die Ergebnisse aus Messungen mit May
Pack-ähnlichen Probensammlern in der Reinluft hinter einem Jodfilter,
durch das die Abluft einer heißen Zelle gefiltert wird, besonders in-
teressant /34/. Es wurden Jodverbindungen mit sehr unterschiedlichem
Abscheidungsverhalten festgestellt. Eine Abhängigkeit von den Reagen-
tien, die in der heißen Zelle bei den Arbeiten zur Abtrennung von
$^{131}$J aus bestrahltem Telluroxid eingesetzt werden, konnte festgestellt
werden. Aehnliche Messungen ergaben eine scheinbare Abhängigkeit des
Abscheidegrades von der Jodkonzentration /31/.

Der Aussagewert von Vor Ort-Prüfungen mit radioaktiv markiertem Methyl-
jodid wurde ebenfalls in Verbindung mit den Betriebsbedingungen, unter
denen die Jodfilter arbeiten, diskutiert:

Vor Ort-Prüfungen können gewöhnlich nur unter normalen Betriebsbedin-
gungen der zu überprüfenden Jodfilteranlage erfolgen. Die Durchlaß-
grade, die bei Verwendung von radioaktiv markiertem Methyljodid als
Prüfmittel bei der Vor Ort-Prüfung gemessen werden, können nur dann
als ausreichend konservativ für die Abscheideleistung des Jodfilters

gegenüber einem Spaltjodgemisch unbekannter Zusammensetzung ange-
sehen werden, wenn sich die ungünstigsten Betriebsbedingungen nicht
wesentlich von den Prüfbedingungen unterscheiden. Zur Beurteilung
der Durchlaßgrade, die unter Reaktor-Störfallbedingungen zu erwarten
sind, muß vor allem der Einfluß der u. U. stark erhöhten relativen
Luftfeuchte berücksichtigt werden. Eine Extrapolation der in Vor Ort-
Prüfungen gemessenen Durchlaßgrade auf erhöhte Luftfeuchten ist mit
großen Unsicherheiten belastet, da:

1. es nicht sicher ist, daß sich die Aktivkohle des Jodfilters mit
   dem Wasserdampfgehalt der anströmenden Luft im Adsorptions-Desorp-
   tionsgleichgewicht befindet. Anderenfalls erlaubt die während der
   Vor Ort-Prüfung leicht durchzuführende Messung der relativen Luft-
   feuchte keine Korrelation zwischen Luftfeuchte und Durchlaßgrad;

2. nicht die gleiche Abhängigkeit zwischen Luftfeuchte und Durchlaß-
   grad der Aktivkohle erwartet werden kann, wie sie sich in Labor-
   versuchen mit unbenutzter Aktivkohle ergeben hat;

3. der durch die Vor Ort-Prüfung ermittelte Durchlaßgrad die Summe
   aus der Leckrate aufgrund mechanischer Lecks und der Sorptions-
   eigenschaften der Aktivkohle wiedergibt und die Beiträge der ein-
   zelnen Effekte nicht ohne wesentlichen zusätzlichen Aufwand ermit-
   telt werden können.

In Vorträgen und in Diskussionen wurde zwar darauf hingewiesen, daß
eine stärkere Alterung und Vergiftung auch bei der Vor Ort-Prüfung
mit radioaktiv markiertem Methyljodid unter normalen Betriebsbedin-
gungen erkennbar ist (siehe z. B. Angaben in /35/ und /15/), eine ge-
sicherte Aussage zum Durchlaßgrad unter Störfallbedingungen bzw. zum
Zustand der Aktivkohle aber nur durch zusätzliche Laborprüfung von
repräsentativen Aktivkohleproben aus dem Jodfilter ermöglicht wird.
Die Entnahme von Proben aus dem Filter ist allerdings häufig nicht
möglich und kann außerdem zu Lecks führen. In einem Vortrag /32/ wur-
de berichtet, daß die während der Vor Ort-Prüfung gemessenen Werte
keinerlei Zusammenhang mit den Ergebnissen der Laborprüfung zeigten.
Dies wurde in der Hauptsache auf das Auftreten von mechanischen Lecks
und Abrieb zurückgeführt und ist dann natürlich verständlich. Die

Kombination verschiedener Einwirkungen auf ein Jodfilter, die nach erheblichen Störfällen auftreten, kann zu Belastungen führen, deren Auswirkung weder aus dem Ergebnis der Vor Ort-Prüfung noch dem Labortest hervorgehen. Eine Typprüfung der Störfall-Jodfilter unter simulierten Störfallbedingungen erscheint deshalb als Ergänzung notwendig. Ein entsprechend ausgerüsteter technischer Filterprüfstand wurde beschrieben /42/.

## Laborprüfung des Jod-Sorptionsmaterials

Die Vorträge zur Prüfung der Aktivkohle im Labortest zeigten völlige Uebereinstimmung in der Wahl von radioaktiv markiertem Methyljodid als Prüfmittel. In Einzelfällen wurde zusätzlich mit radioaktiv markiertem elementarem Jod geprüft. Die beschriebenen Apparaturen ermöglichen durchweg die Prüfung von Jod-Sorptionsmaterialien bei hohen relativen Luft- bzw. Gasfeuchten, die apparative Ausstattung und Instrumentierung variiert allerdings über einen weiten Bereich und es kann nicht ausgeschlossen werden, daß aufgrund derartiger Unterschiede auch unterschiedliche Abscheidegrade für gleiche Aktivkohlen unter vergleichbaren Bedingungen gemessen werden. Als Parameter, der am schwersten einzustellen und zu messen ist, erwies sich die relative Gasfeuchte. Dies gilt besonders dann, wenn Messungen im Bereich hoher Luftfeuchten ($\geqq 95$ % r.F.) durchgeführt werden. Die Diskussion ergab, daß die verschiedenen europäischen Laboratorien an der Durchführung von Vergleichstesten dringend interessiert sind und es wurde sehr begrüßt, daß von seiten der Kommission die Bereitschaft besteht, Vergleichsteste zu organisieren und auszuwerten. Es erscheint sinnvoller, eine Wertung der einzelnen Laborapparaturen vorzunehmen, wenn die Ergebnisse von Vergleichstesten vorliegen.

Uebereinstimmend wurde die Prüfung der Abscheideleistung der Aktivkohle gegenüber radioaktiv markiertem Methyljodid als wesentliche Voraussetzung zur Beurteilung ihrer Verwendbarkeit in Jodfiltern angesehen. Die Prüfung sonstiger Eigenschaften der Aktivkohlen wurde in den Vorträgen nicht behandelt. Die Diskussion zeigte, daß die systematische Messung von Korngrößenverteilung, innerer Oberfläche, Porengröße und Verteilung, Porosität, Härte, Imprägnierung usw. fast aus-

schließlich von den Herstellern der Aktivkohle, und, in geringem Umfang, von den Filterherstellern durchgeführt wird. Nur in Sonderfällen messen auch die Laboratorien, die die Messung der Abscheideleistung der Aktivkohle vornehmen, diese Eigenschaften der Aktivkohle.

Von besonderer Bedeutung für die Abscheideleistung einer bestimmten Aktivkohlensorte ist ihre Korngröße. In der Diskussion wurde darauf hingewiesen, daß die Definition der Grenzkorngrößen allein sich nicht als ausreichend erwiesen hat und die anteilmäßige Verteilung auf einzelne Korngrößenfraktionen innerhalb der angegebenen Grenzen normiert werden sollte. In einzelnen Ländern muß der Anteil der Korngrößenfraktionen innerhalb vorgegebener Bereiche eingehalten werden. Dadurch wird eine Manipulation des Abscheidegrades über die Korngrößenverteilung weitgehend ausgeschlossen.

Vorträge und Diskussion zeigten, daß Laborprüfungen des Jod-Sorptionsmaterials mit radioaktiv markiertem Methyljodid unter sorgfältig ausgewählten und kontrollierten Bedingungen grundsätzlich durchgeführt werden müssen, um :

1. die Eignung von Aktivkohlechargen vor der Verwendung in einem Jodfilter nachzuweisen, da verschiedene Aktivkohlechargen des gleichen Typs vom gleichen Hersteller stark in ihrer Abscheideleistung variieren können.

2. Alterungs- und Vergiftungseffekte während der Einsatzzeit der Aktivkohle in ihrer Auswirkung auf den Abscheidegrad unter ungünstigen Betriebsbedingungen quantitativ erfassen zu können.

Der unter 2. genannte Punkt beeinflußt wesentlich die notwendige Frequenz von Wiederholungsprüfungen.

Zeitabstand zwischen Wiederholungsprüfungen

In einer Reihe von Vorträgen wurde auf die zeitlichen Mindestabstände zwischen Wiederholungsprüfungen an Jodfilteranlagen eingegangen, so z.B. in /28/ und /15/. Einheitliche Meinungen bestehen nicht; über

die Durchführung von Wiederholungstests im Abstand zwischen ca. 2 Monaten und 2 Jahren wurde berichtet. Die Bedeutung, die der Durchführung von Wiederholungsprüfungen zugemessen wird, zeigte sich u.a. in der großen Anzahl der Diskussionsbeiträge.

Zusammengefaßt ergibt sich folgendes Bild:

Der Abscheidegrad von Jodfiltern kann durch äußere Einflüsse, vor allem durch Beladung mit Filterschadstoffen wie Oel und organische Lösungsmittel, in kurzer Zeit herabgesetzt werden. Wiederholungsprüfungen nach starker Einwirkung von Filterschadstoffen bzw. nach Betrieb unter extremen Druck-, Feuchte- und Temperaturbedingungen sind zu fordern. Es besteht jedoch keine Sicherheit, daß derartige Einwirkungen in der Praxis auch in ihrer Bedeutung erkannt werden.

Vorhersagen zum Ausmaß der Schadstoff-Beladung und Vergiftung von Aktivkohlefiltern setzen eine genaue Kenntnis der Menge, Art und des zeitlichen Anfalls von Filterschadstoffen während des Betriebes einer kerntechnischen Anlage voraus. Häufig können solche Voraussagen nicht bzw. nicht mit der erforderlichen Genauigkeit gemacht werden. Jodfilter, die dauernd in Betrieb sind bzw. nach kleinen, während des Reaktorbetriebes häufiger zu erwartenden Zwischenfällen, wie Dampfleckagen mit geringer Aktivitätsfreisetzung, in Betrieb genommen werden, können deshalb unerwartet schnell eine verringerte Abscheideleistung zeigen. Die von unregelmäßig auftretenden Einflüssen unabhängige, experimentell bestimmbare Alterung von Aktivkohle, die auch bei verschlossenen Proben auftritt, dürfte demgegenüber eine wesentlich geringere Bedeutung für den Abscheidegrad haben. In der Summe resultiert also eine Unsicherheit in Hinsicht auf den zu einem bestimmten Zeitpunkt erreichbaren Abscheidegrad, die auch durch häufige Wiederholungsprüfungen nicht vollständig eliminiert werden kann.

Die Notwendigkeit zur Durchführung von Wiederholungsprüfungen hängt von der Betriebsweise des Filters, äußeren Einflüssen und zusätzlich von der Auslegung des Jodfilters ab. Zu berücksichtigen ist dabei vor allem die gegebenenfalls vorhandene Ueberschußmenge an Aktivkohle zum Ausgleich für Alterung und Vergiftung und die Qualität der Konstruktion.

Faßt man die genannten Punkte zusammen, kommt man zwangsweise zu der Aussage, daß eine generelle Festlegung von Prüffrequenzen für Jodfilter nicht möglich ist (z.B. Angaben in /28/ und /40/). Individuelle Festlegungen sollten aufgrund einer Abschätzung der sicherheitstechnischen Konsequenzen eines Absinkens der Abscheideleistung und möglichst bereits vorliegender Prüferfahrung unter Berücksichtigung spezifischer Alterungsversuche getroffen werden /36/. Grundsätzlich sollte die Auslegung von Jodfiltern einen Zuschlag für Alterung und Vergiftung auf die Menge der benötigten Aktivkohle berücksichtigen; die dafür notwendigen Kosten dürften vergleichsweise gering sein gegenüber dem sonst anfallenden Aufwand für zusätzliche Prüfungen. Die Anzahl der Vor Ort-Prüfungen kann beim Vorliegen geeigneter, zuverlässiger Filterkonstruktionen wesentlich dadurch gesenkt werden, daß Proben der Aktivkohle aus den Filtern zwischen solchen Prüfungen im Labor untersucht werden.

In der Diskussion wurde ausdrücklich auf Lüftungskonzepte hingewiesen, bei denen Jodfilter für den Störfall- und den Normalbetrieb konsequent getrennt sind. Dadurch ist mehr Sicherheit gegeben, daß bei Bedarf ein ausreichender Abscheidegrad erreicht wird, denn dieses Konzept schließt eine Vorbeladung von Jodfiltern, die im Störfall für die Begrenzung der Umgebungsbelastung entscheidend sind, weitgehend aus. Außerdem kann, bei nachgewiesener Zuverlässigkeit der Konstruktion, mit einer geringen Prüffrequenz die Abscheideleistung hinreichend sicher gewährleistet werden. Die Auftrennung in Filter für Störfall- und Normalbetrieb setzt eine klare Definition dieser Betriebsarten voraus. Hier ist, wie die Diskussion zeigte, ein weiter Ermessensspielraum gegeben und Festlegungen können nur unter Berücksichtigung des jeweiligen Reaktor- und Lüftungskonzeptes erfolgen.

### Entnahme von Aktivkohleproben aus dem Jodfilter

Wenn keine besonderen konstruktiven Maßnahmen zur Entnahme von Aktivkohleproben aus den Jodfiltern vorgesehen sind, ist die Gewinnung repräsentativer Proben für die Laboruntersuchung meistens nicht möglich. Probenahme aus dem Jodfilter kann außerdem zu Lecks führen. Dies gilt

besonders dann, wenn ganze Aktivkohlefilterzellen ausgebaut werden
müssen, um repräsentative Proben der Aktivkohle entnehmen zu können.
Der Dichtsitz der als Ersatz einzubauenden Aktivkohlefilterzelle kann
oft nur durch eine erneute Vor Ort-Prüfung garantiert werden. Damit
wird der insgesamt notwendige Aufwand für die Beschaffung einer re-
präsentativen Probe der Aktivkohle zu groß. Bei Schüttbettfiltern
können ebenfalls Schwierigkeiten auftreten, weil die Konstruktionen
die Entnahme einer Aktivkohleprobe, die die gesamte Bett-Tiefe des
Jodfilters repräsentiert, gewöhnlich nicht erlauben.

In mehreren Vorträgen wurde über die Anwendung von Einrichtungen be-
richtet, in denen im Bypass zum Jodfilter Aktivkohle aus der Origi-
nalcharge des Filters mit einem Teilstrom der Abluft gleichzeitig mit
dem Jodfilter beaufschlagt wird. Dadurch können, ohne Eingriff in das
eigentliche Jodfilter, repräsentative Aktivkohleproben gewonnen wer-
den. Ein Nachteil der Probenbeaufschlagung im Bypass ist durch die
erhöhte Wahrscheinlichkeit für mechanische Lecks gegeben. Die Bypass-
Probenhalter müssen in ihrer Leckdichtigkeit dem gleichen Standard
entsprechen wie das eigentliche Jodfilter. Da jede zusätzliche Bypass-
Strecke das Leckrisiko erhöht, muß ihre Anzahl und damit die Zahl der
verfügbaren Kohleproben gering gehalten werden. Einmal geprüfte Aktiv-
kohleproben werden gewöhnlich nicht wieder in den Bypass-Probenhalter
eingesetzt. Die Anzahl der verfügbaren Proben ist also von vornherein
festgelegt und es ist, wegen der Unsicherheit in bezug auf die Prüf-
frequenz, nicht sicher, daß die vorgesehene Probenzahl zur Kontrolle
über die gesamte Filterstandzeit ausreicht.

In der Diskussion wurden verschiedene Konstruktionen erwähnt, die ei-
ne Beaufschlagung von Aktivkohleproben im Bypass ermöglichen. Da aber
keine vollständigen Angaben über Anzahl, Konstruktion und Leckdich-
tigkeit gemacht wurden, kann eine vergleichende Wertung z.Z. nicht
durchgeführt werden. In diesem Zusammenhang sei darauf hingewiesen,
daß die in der Bundesrepublik Deutschland verwendeten Bypass-Proben-
sammler, die als "Kontrollfilter" bezeichnet werden, eine Trennung
der Aktivkohle in mindestens zwei aufeinanderfolgende Betten gewähr-
leisten müssen. Dadurch kann das Fortschreiten einer in Anströmrich-
tung über die Bett-Tiefe erfolgenden Vergiftung bei der Laborprüfung

erkannt und die Bett-Tiefe der noch einwandfreien Aktivkohle bei je-
dem Labortest bestimmt werden. Die bisherigen Erfahrungen zeigen,
daß die üblichen Schadstoffe nur langsam in die Tiefe des Bettes hin-
einwandern und nur selten leichtflüchtige Komponenten auftreten, die
z.B. eine 50 cm tiefe Aktivkohleschicht bei einer linearen Luftge-
schwindigkeit von 50 cm/s schnell penetrieren. Als wertvolles analy-
tisches Verfahren zur Aufklärung der chemischen Natur von Filter-
schadstoffen hat sich die Gaschromatographie bewährt.

Ein Aktivkohle-Probensammler einfacher Konstruktion, der die Entnahme
von Kohleproben aus Schüttbett-Filtern horizontaler und vertikaler
Anströmrichtung erlaubt, wurde in /28/, Abb. 8a und 8b beschrieben.
Mit dieser Einrichtung wurden realistische Daten zur Alterung /14/
während des Filterbetriebes gewonnen. Vor Ort-Prüfungen von Filter-
anlagen zeigten /28/, daß durch diese Probensammlerkonstruktion kei-
ne Leckagenprobleme hervorgerufen wurden.

Da die Alterung und Vergiftung von Aktivkohlefiltern heute ein ent-
scheidendes Problem der Jodfilterung darstellt, sollten Jodfilteran-
lagen grundsätzlich mit Einrichtungen zur Gewinnung repräsentativer
Aktivkohleproben ausgerüstet sein. Die Diskussion zeigte, daß das
Vorhandensein solcher Einrichtungen noch nicht überall Stand der
Technik ist.

Erreichbare Abscheidegrade in Jodfiltern

Bisher besteht keine einheitliche Vorstellung darüber, welche Ab-
scheidegrade durch Jodfilter überhaupt erreicht werden sollten. Mit
einer Vergrößerung der Bett-Tiefe ist, zumindest bei Schüttbettfil-
tern, mit relativ kleinem Aufwand eine wesentliche Verbesserung der
Abscheideleistung verbunden und es bleibt etwas der Willkür über-
lassen, welche Forderungen an die Abscheideleistung zu stellen sind.
Dies gilt umso mehr, als für die Abgabe von Aktivität aus Kernkraft-
werken unterhalb gewisser Grenzwerte als Richtschnur nur eine so
strapazierbare Formulierung wie "so niedrig, wie mit technisch sinn-
vollem Aufwand erreicht werden kann" gegeben ist. Bei der Frage,
welches der Mindestabscheidegrad ist, bei dessen Unterschreitung ein
Jodfilter ausgewechselt werden sollte, wird man sich gewöhnlich an

den in den Genehmigungsunterlagen festgelegten Abscheidegraden orien-
tieren. Diese müssen aber durchaus nicht dem Stand der Technik ent-
sprechen. Eine Umfrage unter den Vortragenden ergab, daß ein Mindest-
dekontaminationsfaktor von 1000 für radioaktives Jod und radioaktives
Methyljodid als sinnvoll angesehen wird, wenn es sich um Jodfilter
zur Abluftfilterung handelt.

Bei Verwendung von Jodfiltern mit geringer Bett-Tiefe (bzw. geringer
Verweilzeit) kann ein DF von 1000 für Methyljodid bei hoher relativer
Gasfeuchte nicht oder nicht mit genügender Sicherheit erreicht werden.
Die relativ niedrigen Werte, die von der USAEC in Ansatz gebracht
werden /17/, reflektieren diese Situation.

Die Festlegung des nachzuweisenden Dekontaminationsfaktors für eine
Jodfilteranlage erfordert eine Definition der Zusammensetzung des Ge-
misches von Jodverbindungen, die in der Filterzuluft angenommen wer-
den. Einige Angaben dazu konnten der Diskussion entnommen werden. Zur
Zeit wird in Deutschland eine Jodzusammensetzung im Sicherheitsbe-
hälter nach einem schweren Reaktorstörfall von 85 % elementarem Jod,
10 % Methyljodid und 5 % an Partikel gebundenem Jod angenommen, wäh-
rend im USAEC Regulatory Guide 1.52 91 % elementares Jod, 4 % Methyl-
jodid und 5 % partikelförmiges Jod zugrundegelegt werden.

Zusammenfassung

Die Betriebserfahrungen und die Prüfergebnisse, die an Jodfilteranla-
gen gewonnen wurden, zeigen, daß hohe Abscheidegrade bei einwandfreiem
mechanischen Aufbau der Filter und Verwendung von imprägnierten Aktiv-
kohlen erreicht werden können.

Ueber das Auftreten von mechanischen Lecks in den Filteranlagen wurde
häufig berichtet, jedoch geht aus den Vorträgen deutlich hervor, daß
geeignete Konstruktionen existieren, die praktisch kein Leck zeigten
und sich die Ursachen für Leckagen, seien sie gegeben durch undichte
Schweißnähte, mangelhafte Absperrventile im Bypass, Verlust an Aktiv-
kohle durch unzureichende Halterung, Abrieb oder durch Nachsacken,
mit entsprechendem Aufwand abstellen /28/ /27/ /15/ bzw. vermeiden
lassen.

Die Mehrzahl der Vorträge ließ erkennen, daß das Problem der Alterung und Vergiftung der Aktivkohle während der Einsatzzeit im Jodfilter zwar erkannt, aber weitgehend ungelöst ist und aufgrund dieser Effekte eine erhebliche Unsicherheit in bezug auf die zu einer bestimmten Zeit zu erwartende Abscheideleistung besteht. Nur bei Abwesenheit von Vergiftungseffekten könnte das Absinken der Abscheideleistung, wie durch die britischen Autoren angegeben /14/, vorausberechnet werden. Ueber die Vergiftung der Aktivkohle mit aliphatischen Verbindungen /28/ /29/, Oel und Lösungsmitteln wurde berichtet, gaschromatographische Untersuchungsmethoden zur Aufklärung der Art der Filterschadstoffe wurden herangezogen /15/. Es wird ein erheblicher Aufwand in Form von Laborprüfungen an Proben der Originalkohle aus den Jodfiltern bzw. an Proben, die im Bypass beaufschlagt wurden, getrieben, ohne daß mit befriedigender Sicherheit Aussagen zur Abscheideleistung der Jodfilter über längere Betriebsperioden gemacht werden können.

Jodfilter mit großer Bett-Tiefe, die einer hohen Verweilzeit entspricht, zeigen vergleichsweise bessere Standzeiten, da Filterschadstoffe bereits durch Aktivkohleschichten geringer Tiefe abgeschieden werden, falls sie keine zu große Flüchtigkeit besitzen. Eine vollständige Trennung von Störfallfiltern und Filtern, die im Normalbetrieb eingesetzt werden, bietet ebenfalls ein erhöhtes Maß an Sicherheit, da dann zur Beherrschung von Unfallfolgen ein von Vorbeladung weitgehend freies Jodfilter zur Verfügung steht.

Die vorgetragenen Daten zum Betriebsverhalten von Jodfiltern sollten zum Anlaß genommen werden, wesentliche Arbeit in die Entwicklung von Jod-Sorptionsmaterialien mit verbesserter Beständigkeit gegenüber Alterung und Vergiftung zu investieren und außerdem Untersuchungen zur Schadstoffabscheidung aus der Filterzuluft aufzunehmen.

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BIBLIOGRAPHY *)

/1/ J.G. WILHELM, Seminar vol. I, pp. 1-24

/2/ D.T. PENCE, W.J. MAECK, Proceedings of the 11th AEC Air
Cleaning Conf., Washington 1970, p. 467

/3/ W.J. MEGAW, F.G. MAY, The behavior of iodine released of
reactor containers, J. Nucl. Energy, 16, pp. 427-435, 1962

/4/ A.E.J. EGGLETON, D.H.F. ATKINS, Identification of radioiodine
compounds formed on releasing carrier free I-131 in air,
Trans. Am. Nucl. Soc., 6, pp. 129-130, 1963

/5/ A.E.J. EGGLETON, D.H.F. ATKINS, The identification of trace
quantities of radioactive iodine compounds by gas chromato-
graphic and effusion methods, Radiochimica Acta, 3,
pp. 151-158, 1964

/6/ F.O. CARTAN, H.R. BEARD, F.A. DUCE, J.H. KELLER, Proceedings
of the 10th Air Cleaning Conf., 1968, p. 342

/7/ K. PFEIFFER, Seminar vol. I, pp. 95-119

/8/ J. BARBIER, Seminar vol. I, pp. 71-93

/9/ D.A. COLLINS, A.E. McINTOSH, R. TAYLOR, W.D. YUILLE, Experi-
ments relating to the control of fission-product release from
advance gas-cooled reactors, J. Nucl. Energy, Parts A/B,
vol. 20, pp. 97-122, 1966

/10/ J.J. HILLARY, Seminar vol. I, pp. 25-36

/11/ J.J. HILLARY, J.C. TAYLOR, Seminar vol. I, pp. 37-51; also
issued as TRG Report 2433 (W), UKAEA

/12/ J. BARBIER, G. BENEZECH, B. CADET, J. MIRIBEL, P. SIGLI,
Seminar vol. I, pp. 53-69

/13/ A.K. POSTMA, R.W. ZAVADOSKI, Review of organic iodide form-
ation under accident conditions in water-cooled reactors,
WASH-1233 (Oct. 1972)

/14/ L.R. TAYLOR, R. TAYLOR, Seminar vol. I, pp. 121-148; also
issued as TRG Report 2483 (W), UKAEA

/15/ J.G. WILHELM, K. GERLACH, Seminar vol. I, pp. 465-481

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*) In this list quotation to papers presented at the "Seminar on
Iodine Filter Testing", Karlsruhe, 4-6 December 1973 and pub-
lished in the Proceedings is abbreviated by "Seminar vol. I,
pp. ...".

/16/ C.A. BURCHSTED, A.B. FULLER, Design, Construction and Testing
of High Efficiency Air Filtration Systems for Nuclear Appli-
cation, ORNL - NSIC - 65 (January 1970)

/17/ R. ZAVADOSKI, Seminar vol. I, pp. 547-563

/18/ M. BELVAL, J. MIRIBEL, Seminar vol. I, pp. 199-210

/19/ J. FURRER, J.G. WILHELM, Seminar vol. I, pp. 185-198

/20/ A.G. EVANS, Effect of Intense Gamma Radiation on Radioiodine
Retention by Activated Carbon, 12th USAEC Air Cleaning
Conference 1972, CONF-720823, p. 401

/21/ R.A. LORENZ, W.G. MARTIN, ORNL-TM-3973, p. 142

/22/ RDT Standard M-16-IT "Gas-Phase Adsorbents for Trapping Radio-
Iodine and Iodine Compounds", USAEC Div. of Reactor Develop-
ment and Technology (June 1972)

/23/ AACC CS-8T "Tentative Standard for High-Efficiency Gas-Phase,
Adsorbent Cells", Amer. Ass. for Contamination Control,
July 1972

/24/ F. HERRE, Seminar vol. I, pp. 175-184

/25/ H.J. STRAUSS, G. STASCHIK, K. WINTER, Seminar vol. I,
pp. 163-173

/26/ F.H. PASSANT, Seminar vol. I, pp. 149-162

/27/ M. STEAD, Seminar vol. I, pp. 391-404

/28/ J.J. HILLARY, L.R. TAYLOR, Seminar vol. I, pp. 361-390;
also issued as TRG Report 2497 (W), UKAEA

/29/ J.J. CLIFTON, Seminar vol. I, pp. 405-414

/30/ N. FIORENTINO, S. MALOSSI, G. MESSORE, G. SACCO, Seminar
vol. I, pp. 431-463

/31/ G. SCHULZE-PILLOT, Seminar vol. I, pp. 483-488

/32/ M. GENCE, Seminar vol. I, pp. 415-430

/33/ J.R.D. STOUTE, G.C.H. GROEN, Seminar vol. I, pp. 503-509

/34/ G. FIEUW, R. BOULENGER, Seminar vol. I, pp. 489-502

/35/ R. HESBÖL, B. NORMANN, L. DEVELL, Seminar vol. I,
pp. 329-351

/36/ J.G. WILHELM, H.G. DILLMANN, K. GERLACH, Seminar vol. I,
pp. 211-235

/37/ J.J. HILLARY, Seminar vol. I, pp. 237-257

/38/ P. SIGLI, L. TREHEN, Seminar vol. I, pp. 259-269

/39/ N. FIORENTINO, S. LANZA, S. MALOSSI, M. MAZZINI, G. MESSORE, Seminar vol. I, pp. 271-313

/40/ G. van der LUGT, L.C. SCHOLTEN, Seminar vol. I, pp. 315-327

/41/ D.R. MUHLBAIER, Standardized nondestructive test of carbon beds for reactor confinement application, USAEC Report DP-1082 (July 1967)

/42/ H.G. DILLMANN, F. BRUEDERLE, J.G. WILHELM, Seminar vol. I, pp. 353-360

/43/ R.W. ZAVADOSKI, H. GILBERT, A.B. FULLER, C.A. BURCHSTED, Engineered Safety Features Air Cleaning Systems for Commercial Light-Water-Cooled Nuclear Power Plants, WASH-1234 (June 1974)

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LABORATORIES PARTICIPATING IN THE INTERCOMPARISON
TEST PROGRAMME FOR IODINE SORBENT MATERIALS


Belgium                    – S.C.K./C.E.N. Dep. Met. en Kontr. Stral.
                             Mol


France                     – C.E.A. – STEPPA
                             Fontenay–aux–Roses


Germany                    – Kernforschungszentrum
                             Abt. Strahlenschutz und Sicherheit
                             Karlsruhe


Italy                      – Istituto di Impianti Nucleari
                             Università di Pisa


Netherlands                – N.V. KEMA
                             Arnhem

                           – R.C.N. – G.B.A.
                             Petten


Sweden                     – Aktiebolaget Atomenergi
                             Health and Safety Section
                             Studsvik
                             Nyköping


United–Kingdom             – Reactor Development Laboratory
                             Windscale Works
                             Seascale


Some laboratories overseas have also expressed their interest in parti-
cipating in this test programme.

# BEHAVIOUR OF IODINE SORPTION MATERIALS

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SUMMARY. All iodine compounds to be found in the air vented from nuclear power plants are given. The chemical reactions by means of which fission-product iodine is retained by the sorption materials used nowadays, are explained briefly.
The importance of the main parameters affecting the layout of sorption beds, such as type and grain size of the sorption material and relative humidity and temperature of the carrier gas, are discussed with reference to experimental results. Experiences on the dependence of the retention efficiency on the concentration of elementary iodine and methyl-iodide in the air are reported.
The results are given of service life experiments on the ageing and poisoning of the sorption material and measures to prolong service life are discussed.

KURZFASSUNG. VERHALTEN VON JOD-SORPTIONSMATERIALEN. Es werden die Jod-verbindungen angegeben, die in der Abluft von Kernkraftwerken zu erwarten sind. Die chemischen Reaktionen, durch die Spaltjod an den heute verwandten Sorptionsmaterialien abgeschieden wird, werden kurz erläutert.
Die Bedeutung der wichtigsten Einflussgrössen für die Auslegung der Sorptionsbetten, wie Art und Korngrösse des Sorptionsmaterials sowie relative Feuchte und Temperatur des Trägergases wird aufgrund experimenteller Ergebnisse diskutiert. Ueber einige Untersuchungen zur Abhängigkeit des Abscheidegrades von der Konzentration an elementarem Jod und Methyljodid in der Raumluft wird berichtet.
Die Ergebnisse von Standzeituntersuchungen zur Alterung und Vergiftung des Sorptionsmaterials werden wiedergegeben und Massnahmen diskutiert, die zur Verlängerung der Einsatzzeit führen.

RESUME. COMPORTEMENT DES MATERIAUX UTILISES POUR LA SORPTION DE L'IODE.
Les composés iodés auxquels on peut s'attendre dans l'air sortant de centrales nucléaires sont indiqués. Les réactions chimiques par lesquelles on sépare l'iode de fission dans les matériaux de sorption actuellement utilisés sont brièvement expliquées.
En se basant sur des résultats d'expérience, on discute de la significa-tion des paramètres les plus importants pour la conception des filtres à sorption, tels que la nature et la granulométrie des matériaux de sorption ainsi que l'humidité relative et la température du gaz porteur. Il est rendu compte de quelques expériences portant sur la dépendance du taux de séparation en fonction de la concentration de l'iode élémentaire et de l'iodure de méthyle dans l'air ambiant. On communique les résultats d'exa-mens de longue durée relatifs au vieillissement et à l'empoisonnement des matériaux sorbants, et on discute des mesures destinées à en prolonger leur durée d'emploi.

1. Introduction

Iodine occupies a special position among the fission products that may
be released during the operation and as a consequence of incidents of
nuclear power stations or reprocessing plants. This is due to the high
fission yield of specific iodine isotopes, the volatility of elemental
iodine and many iodine compounds, the half-lives of various iodine iso-
topes, such as ^{131}I and [129]I, which are sufficiently long to extend over
prolonged transport periods, and the retention and enrichment in the
human body, especially in the thyroid.

Today, iodine filters are among the usual safety facilities of nuclear
power stations. In general, calculations of the expected environmental
exposure indicate that decontamination factors of gaseous effluents
between $10^2$ and $10^3$ will sufficiently reduce the release of iodine.
The removal efficiency of fission product iodine filters is a func-
tion of many parameters, the most important of which will be outlined
very briefly below.

2. Types of Fission Product Iodine

Fission product iodine that has been released into the environment may
occur in various airborne forms whose percentage fraction of the total
amount of fission product iodine released varies within broad limits
and depends on the conditions during release and on the transport path.
According to the present state of knowledge, it is above all elemental
iodine, methyl iodide from the reaction of organic impurities of the
air with iodine, and iodine bound to particles which must be conside-
red in designing iodine filters (1, 2). Other inorganic gaseous iodine
compounds, such as hydrogen iodide and organic iodine compounds of
higher molecular weights, must be expected to occur.

Because of the low mass concentrations of iodine to be expected in the
ventilation air and in the gaseous effluents of nuclear facilities,
both elemental iodine and methyl iodide, as a result of the relatively
high partial vapor pressures, occur practically only as gases even at
room temperature. Particles containing iodine either consist of iodine
compounds of very low vapor pressure (such as a number of metal io-
dides) or iodine adsorbed to particles of other materials. Accordingly,
iodine filters always consist of at least one aerosol filter and one

filter for sorption of gaseous forms of iodine. This seminar deals main-
ly with the removal of gaseous iodine.

A working hypothesis that can be established for safety considerations
assumes that the airborne  iodine present in the containment building
of a water cooled reactor after an incident consists of 85 % elemental
iodine, 10 % organic iodine compounds and 5 % aerosols. In gas cooled
reactors a much higher fraction of iodine must be anticipated to occur
as methyl iodide and iodine bound to particles. This aspect will be
dealt with in more detail in the next few papers (see Seminar vol. I).

Since elemental iodine is partly retained on the surfaces of rooms and
installations, the walls of ventilation ducts etc. by adsorption and
chemisorption,  respectively, it may be expected that the fraction of
highly volatile,relatively inert iodine compounds, such as methyl iodide,
increases in relative proportion to the total amount of  airborne  iodine
with increasing distance from the point of release of fission product
iodine. In addition, the fraction of elemental iodine converted into
iodine compounds by a chemical reaction increases with the stay time
in the air; there also exists a possibility for elemental iodine, after
adsorption on surfaces, to form a highly volatile chemical compound,
which will return to the atmosphere by way of desorption.

It should be indicated that various measurements seem to indicate the
existence of additional gaseous iodine compounds which are retained by
the iodine sorption materials now known with a very low removal effi-
ciency only. The fraction in airborne iodine of such iodine compounds
as a rule is very small and hardly gives rise to the assumption that
iodine compounds which cannot be adsorbed by specially developed sorp-
tion materials with extremely large inner surfaces or cannot be bound
to the impregnation of the iodine sorption material by chemisorption
or isotopic exchange, will be retained largely in the human body or,
e.g. on the grass. Nevertheless, the type and the reaction behaviour
of these persistent iodine compounds should be elucidated to allow
suitable sorption materials to be developed and any conversion into

easily removed or incorporated compounds during transport to be safely
excluded.


3. Iodine Sorption Materials

Elemental iodine can be retained in activated charcoal with high remo-
val efficiencies by means of adsorption and chemisorption. Organic
iodine compounds, such as methyl iodide, are adsorbed to a much lesser
extent, especially in the presence of high relative humidities of the
air accompanied by an adsorption of water vapor.

Fig. 1 shows the penetration of $^{131}$I present as elemental iodine
(bottom curve) and methyl iodide (top curve) into a bed of unimpregna-
ted charcoal. Activated charcoal (from an iodine filter) was taken to
a water–vapor adsorption equilibrium with air of 70 % relative humidity
and afterwards exposed to radioactively labelled $I_2$ and $CH_3I$, respecti-
vely, in air of the same relative humidity. The plot shows the pene-
tration as a function of the depth of bed and the stay time, respecti-
vely. While $^{131}$I as  methyl iodide was practically not retained at all,
the curve for the $I_2$–penetration shows a steep removal profile indi-
cated by a straight line in the semi-logarithmic plot up to a depth
of bed of approximately 2 cm which bends off below a penetration of
approximately 0.1 %. This indicates that elemental iodine (straight
section of curve) had been contaminated by one or more iodine com-
pounds which determined the removal behaviour of the residual activity
after removal of the elemental iodine and could not be removed by
filtering through the existing activated charcoal. Most probably, these
are methyl iodide or similar iodine compounds, small fractions of which
were generated during the production of iodine or during transport.
Because of the high chemical reactivity of elemental iodine a certain
fraction of iodine compounds will practically always be present in
iodine vapor. The amount of this fraction varies with the quality of
the $I_2$–preparation and the humidity of the air. This makes unimpre-
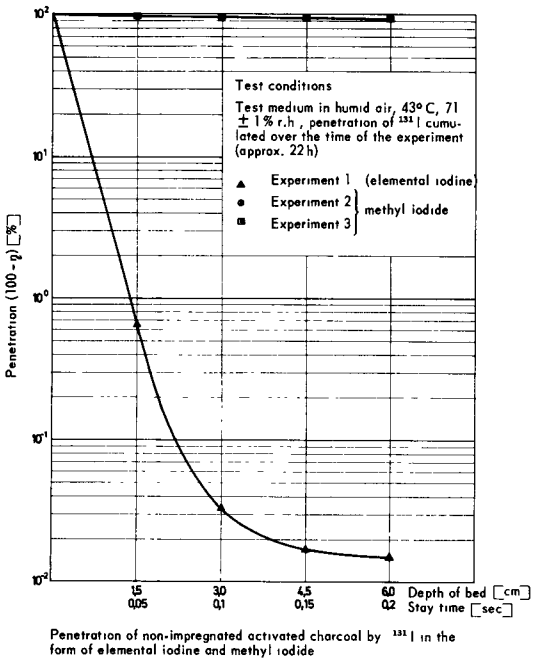gnated activated charcoal unsuitable for iodine removal from humid air.

Test conditions

Test medium in humid air, 43° C, 71 ± 1 % r.h , penetration of $^{131}$I cumulated over the time of the experiment (approx. 22 h)

▲ Experiment 1 (elemental iodine)

● Experiment 2 } methyl iodide

■ Experiment 3

Penetration $(100 - \eta)$ [%]

| 15 0,05 | 30 0,1 | 4,5 0,15 | 60 0,2 | Depth of bed [cm] Stay time [sec] |

Penetration of non-impregnated activated charcoal by $^{131}$I in the form of elemental iodine and methyl iodide

Fig. 1

Impregnations of activated charcoal suitable for the removal of methyl iodide can be brought about by inactive iodine and iodine salts (3, 4) and by tertiary amines, such as triethylene diamine (5).

Since activated charcoal cannot be used at high temperatures and in $NO_x$-bearing gaseous effluents, other sorption materials were developed on the basis of inorganic substances. Silver wire or silver plated copper wire will remove elemental iodine with high efficiencies if the metal surfaces are fresh, but they fail with respect to iodine present as methyl iodide. If the silver is incorporated in molecular sieves, e.g. in the Linde 13 X molecular sieve, and then activated, it is a good reactant also for the removal of iodine present as methyl iodide (6, 7). Molecular sieves containing silver also lend themselves well to the use as iodine sorption materials at high temperatures. However, this material is very expensive because satisfactory removal efficiencies require high silver contents and it is mainly the silver contained in the external layers which will react during the usual short stay times.

Other non-burnable materials which can be used to remove iodine and methyl iodide are produced on the basis of silicic acid or aluminum oxide and impregnated with silver nitrate. One example is the iodine sorption material called AC-6120 developed jointly by the Gesellschaft für Kernforschung and Bayer, Leverkusen (8, 9). This material uses a relatively small amount of silver and yet achieves high removal efficiencies. In addition, it can be employed even in $NO_x$-bearing gaseous
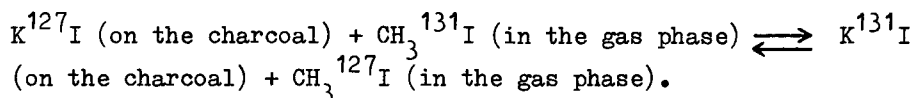
effluents of reprocessing plants.

## 4. Removal Reactions of Iodine Sorption Materials

Elemental iodine is removed by activated charcoal through adsorption
and chemisorption. Because of the positive adsorption behaviour of
elemental iodine, the porous structure and the extremely large inner
surface of the activated charcoal used (approximately 800 – 1,000 $m^2/g$
according to BET), the adsorption process is an important mecha-
nism of removal of elemental iodine; due to the high adsorption of
elemental iodine on the surface of the activated charcoal, this sorption
material removes elemental iodine with high efficiencies even in humid
air.

The adsorption of methyl iodide onto activated charcoal is so strong-
ly impaired by the simultaneous adsorption of water vapor from humid
air that unimpregnated activated charcoal will no longer produce ade-
quate removal efficiencies at humidities of the air $>$ 30 % r.h.;
rising temperatures and humidities of the air will shift the adsorption-
desorption equilibrium even more towards the unfavourable side.

$^{131}$I present as methyl iodide is bound to the present type of iodine
filter charcoal by isotopic exchange (3, 4) or by formation of quaterna-
ry ammonium salts. For isotopic exchange the activated charcoal is im-
pregnated with large amounts (0.5 – 5 wt. %) of inactive iodine or
iodine salts ($^{127}I_2$, $K^{127}I$). The following exchange process occurs
(which is formulated here with $^{131}$I, the iodine isotope most critical
for safety considerations, but also applies to all the other iodine isotopes) :

$K^{127}I$ (on the charcoal) + $CH_3^{131}I$ (in the gas phase) $\rightleftharpoons$ $K^{131}I$
(on the charcoal) + $CH_3^{127}I$ (in the gas phase).

So, radioactive methyl iodide practically enters the bed of activated
charcoal and leaves it again as inactive methyl iodide. Hydrolysis and

adsorption occur as additional less important removal mechanisms. The
process determining the rate of isotopic exchange is the adsorption
and desorption of methyl iodide on the surface of the activated char-
coal. The decontamination factor attainable by the isotopic exchange
is determined by the ratio between inactive $^{127}I$ and $^{131}I$ on the sur-
face of the activated charcoal. Impregnation of the activated charcoal
with large quantities of $^{127}I$, which are opposed to small quantities
of adsorbed $^{131}I$, shifts the point of equilibrium in the reaction quoted
above considerably to the right hand side. Given a sufficiently high
reaction rate and sufficiently long stay time, respectively, of the
gaseous effluent in the activated charcoal, high decontamination fac-
tors can be achieved.

Another very successful impregnating agent for the removal of methyl
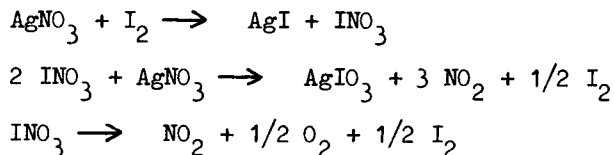iodide is triethylene diamine :
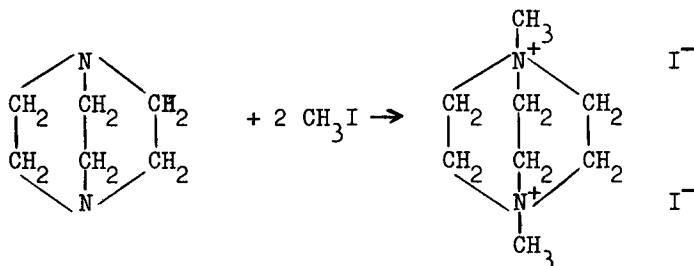


In this case, the removal effect is based on the binding of methyl
iodide in the form of the quaternary ammonium salt formed from
triethylene diamine and methyl iodide being bound to charcoal. Some
of the reactions formulated for methyl iodide also apply to other
organic iodine compounds, such as higher alkylhalides.

Silver incorporated in molecular sieves reacts with elemental iodine
to produce silver iodide. Methyl iodide is also reacted into AgI, the
reaction products having been determined to be dimethyl ether and
methanol (10).

Silver nitrate impregnated on $SiO_2$ and $Al_2O_3$ carrier materials reacts

with elemental iodine, probably according to the following reactions
(11, 12) :

$$AgNO_3 + I_2 \longrightarrow AgI + INO_3$$
$$2\ INO_3 + AgNO_3 \longrightarrow AgIO_3 + 3\ NO_2 + 1/2\ I_2$$
$$INO_3 \longrightarrow NO_2 + 1/2\ O_2 + 1/2\ I_2$$

Accordingly, the iodine is bound as silver iodide and silver iodate.

Methyl iodide and other alkylhalides react with the silver nitrate
impregnation according to the formula (13, 14) :

$$AgNO_3 + R - I \longrightarrow (NO_3 . RI . Ag) \longrightarrow RNO_3 + AgI,$$
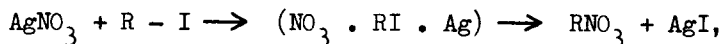
also producing silver iodide.

The final products of the reaction of iodine or methyl iodide with
silver and silver nitrate, respectively, are extremely stable. This
makes materials impregnated in this way particularly suitable for the
removal of gases at higher temperatures or in cases in which a large
amount of decay heat is released in the iodine sorption material.

5. Influence of Silver Content on the Removal Efficiency of Inorganic
   Iodine Sorption Materials

Because of the high price of silver the relation between the silver
content and the removal efficiency of an inorganic sorption material is
a very important factor.

In Fig. 2 the removal efficiencies achieved by the Linde 13 X molecular
sieve in the silver form (LMS 13 X Ag, pellet diameter : 1/16") for
$^{131}I$ as methyl iodide are plotted as a function of the silver
content. The curves were determined for a linear air velocity of 25 cm/s
of the humid air (30° C, 70 % r.h.). A very marked decrease of removal
efficiency with decreasing silver content and a fraction of non-reacting
silver were found. A maximum possible silver content (more than 1/3 of
the weight of the sorption material) is necessary to achieve satisfac-
tory removal efficiencies.

Test conditions:

Humid air, 30° C, 70 % r.h.
Conditioning ≥ 20 h
CH₃I loading ≤ 350 μg/g
(calculated for 10 cm depth of bed)
CH₃I loading period: 1 – 2 h
Sweeping time: 20 - 22 h

O   =   2.5 cm depth of bed
×   =   5.0 cm depth of bed
□   =   7.5 cm depth of bed
▼   =   10.0 cm depth of bed
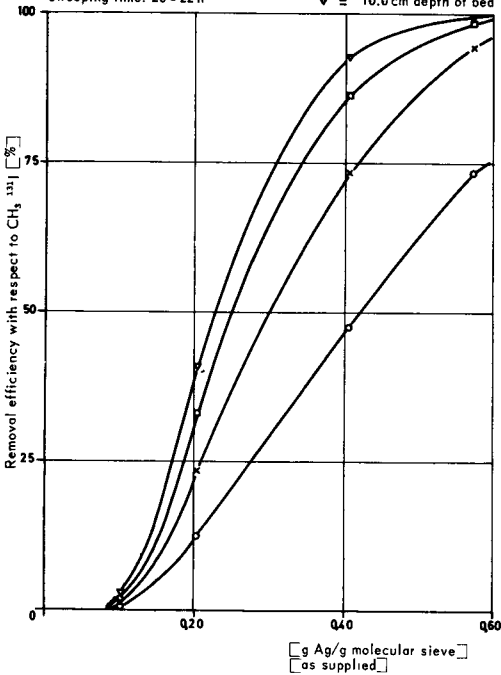
Removal efficiencies with respect to CH₃ ¹³¹I achieved by Linde 13 X Ag molecular sieves as a function of Ag impregnation, 70 % r h.

Fig. 2

Test conditions:

Humid air, 30° C, 70 % r h.
Conditioning ≥ 20 h
CH₃I loading· 1.5 ± 0.5 mg/g
(calculated for 10 cm depth of bed)
CH₃I loading period. 1 h
Sweeping time with humid air. ≥ 20

O   =   2.5 cm depth of bed (AC  6120)
×   =   5.0 cm depth of bed (AC  6120)
□   =   7.5 cm depth of bed (AC  6120)
▼   =   10.0 cm depth of bed (AC  6120)
●   =   10.0 cm depth of bed (Zeolite)
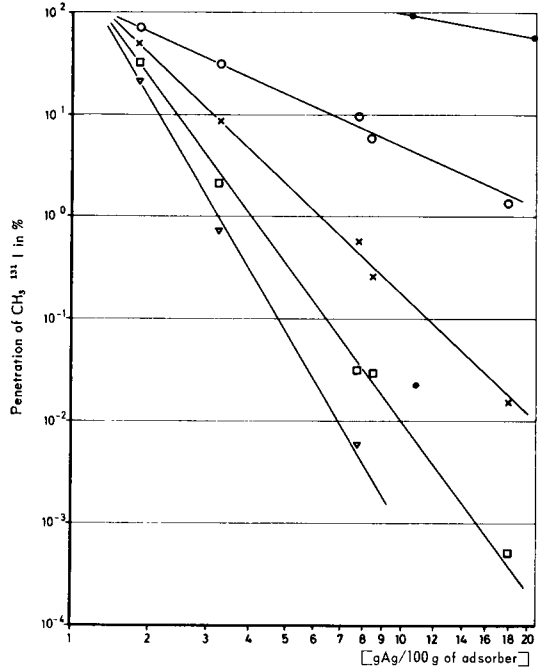
Penetration of AgNO₃ – impregnated adsorbers by CH₃ ¹³¹I as a function of Ag impregnation

Fig. 3

Fig. 3 shows the penetration of AC–6120 as a function of the silver content under the conditions quoted for the experiments in Fig. 2. The same removal efficiencies are achieved with much smaller quantities of silver. The top curve in Fig. 3 applies to LMS 13 X Ag with a silver content in the range indicated and allows a comparison of the removal efficiencies to be made for the same amounts of silver used. It should be borne in mind that LMS 13 X Ag of the pellet type used (diameter 1/16") produces but one third of the pressure drop of AC-6120 (spheres, diameter 1 – 2 mm) at the same depth of bed and linear air velocity. If a correction to the same pressure drop is made by reducing the depth of bed, there is still a removal efficiency which is better by more than one order of magnitude.

## 6. Influence upon the Removal Efficiency of the Grain Size and the Shape of the Iodine Sorption Material

The grain size and the shape of the particles of an iodine sorption material greatly influence the removal efficiency. A reduction in grain size of the same material results in much higher removal efficiencies; in addition, shapes offering a maximum surface relative to the volume have a positive influence upon the removal performance (15, 16).
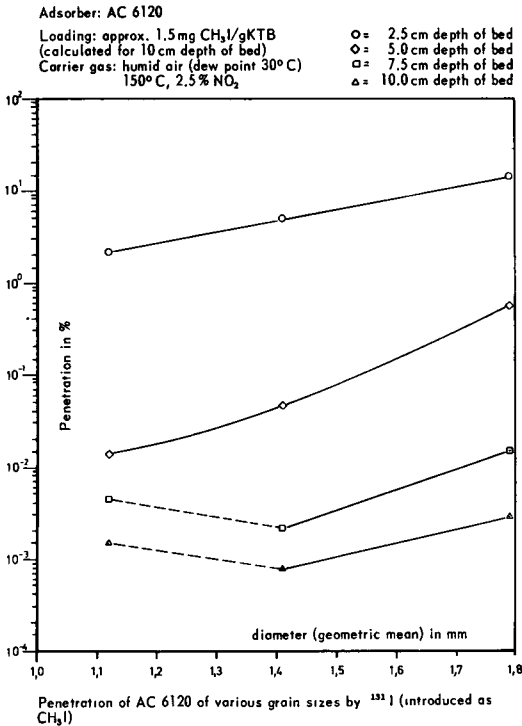


Adsorber: AC 6120
Loading: approx. 1.5 mg $CH_3I$/gKTB (calculated for 10 cm depth of bed)
Carrier gas: humid air (dew point 30° C) 150° C, 2.5 % $NO_2$

O = 2.5 cm depth of bed
◇ = 5.0 cm depth of bed
□ = 7.5 cm depth of bed
△ = 10.0 cm depth of bed

Penetration in %

diameter (geometric mean) in mm

Penetration of AC 6120 of various grain sizes by $^{131}$I (introduced as $CH_3I$)

Fig. 4

Fig. 4 shows the penetration to $^{131}$I administered as methyl iodide of test beds of various grain size fractions of AC–6120. At a depth of bed of 5 cm a 40 % reduction in diameter of the spheres of the iodine sorption material reduced penetration by almost two orders of magnitude. (The apparent increase in penetration in the curves for 7.5 and 10.0 cm depth of bed is probably due to contamination of the test agent by components difficult to remove which had a decisive influence upon the removal profile after more than 99.99 % of the test agent had been filtered out).

In order to compare removal efficiencies of an iodine sorption material the particle diameter and particle shape must also be considered. Since the pressure differential produced across the filter at a specific volume flow is a factor of great importance in the design of a filter system, the removal efficiencies of various iodine sorption materials should be converted, for comparison purposes, to depths of bed resulting in the same differential pressures.

7. <u>Influence of Relative Humidity of the Carrier Gas upon the Removal</u>
<u>Efficiency of Iodine Sorption Materials</u>

The adsorption of iodine and methyl iodide is impeded by water adsorbed
simultaneously. As a function of the relative humidity of gas (air),
the surface of the charcoal is increasingly loaded with water due to
adsorption of single water molecules and aggregations of mono–molecular
and poly–molecular layers and, at extremely high humidities of the air,
due to capillary condensation. The larger pores of activated charcoal
are not filled with water even at 100 % relative humidity of the air.

The adsorption of water in the sorption material above all influences
the removal of radioactive iodine present as methyl iodide. In Fig. 5
the penetration of iodine impregnated activated charcoal by $^{131}I$
administered as methyl iodide is plotted as a function of the depth
of bed. Experiments were performed on humidified and dry activated
charcoal as the sorption materials and humid and dry air as the carrier
gases of the methyl iodide. The curves show that the iodine penetration
of the impregnated activated charcoal after humidifying (water–vapor
adsorption equilibrium set at 98 – 100 % r.h. and 30° C) was practi-
cally the same in dry air ($\leqslant$ 30 % r.h.) and in humid air (98 – 100 %
r.h.), until very low degrees of penetration have been reached.

If dry activated charcoal is exposed to methyl iodide in humid air for
short periods of time (to prevent larger quantities of water from being
adsorbed on to the activated charcoal), much lower penetrations result,
but the curve shows a bend after the largest fraction of the activity
has been removed. A reaction of a small fraction of methyl iodide with
the water vapor of the air into a compound hard to remove must be assu-
med. The same phenomenon can also be found in the removal experiment
conducted in air of high humidity and with humidified activated char-
coal.
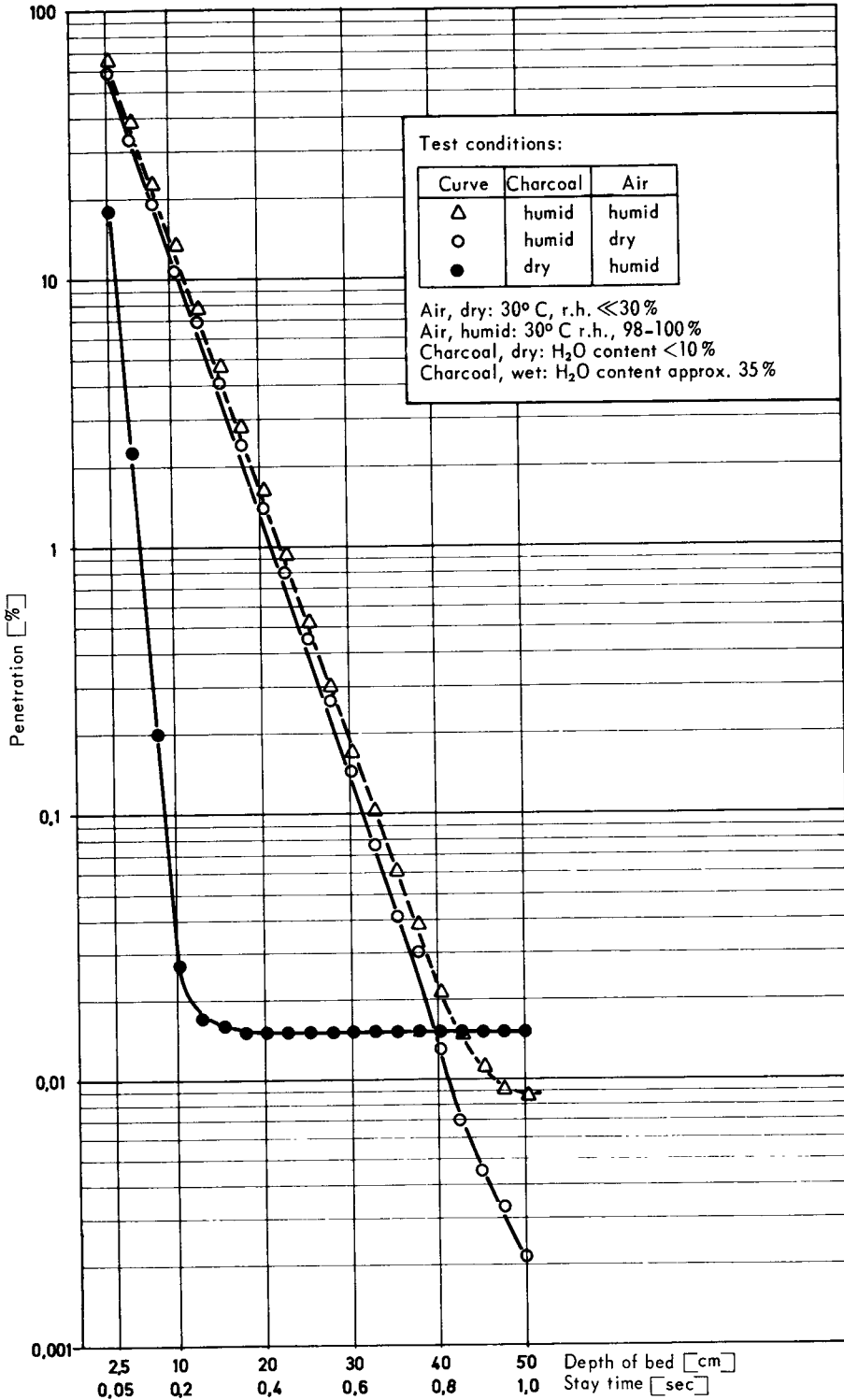
Penetration of activated charcoal beds by [131] I (introduced as CH₃ I) under various humidity conditions of activated charcoal and air

Fig. 5

Experiments performed on dry activated charcoal and dry air (not shown
in the diagram) also resulted in high removal efficiencies of the acti-
vated charcoal. Relative to the humid air exposure case, the curve
showed a bend at a larger bed depth so that, on the whole, a lower
penetration was achieved over the corresponding depth of bed of the
activated charcoal.

The removal efficiency of iodine filters can be described as follows
on the basis of curves shown in Fig. 5 :

– Adsorption of water vapor onto the activated charcoal results in
  increased penetration.

– A filter conditioned by adsorbed water will remove radioactive iodine
  present as methyl iodide with a reduced removal efficiency also from
  dry air.

– If a dry activated charcoal filter is exposed to radioactive methyl
  iodide in humid air, a high initial removal efficiency may be expected
  which will decrease only as the adsorption of water onto the activated
  charcoal increases.

– Removal efficiency for methyl iodide will be lowest with wet charcoal
  and in the presence of air of high humidity.

  Other removal experiments not outlined in the text furthermore indi-
  cate :

– Activated charcoal whose macropores were filled by condensed water
  (e.g., because the temperature in the activated charcoal had fallen
  below the dew point) loses its capability to remove fission product io-
  dine in the form of methyl iodide with a sufficient removal efficiency.

Fig. 6 shows the removal efficiencies achieved by activated charcoal
beds of various depths in the presence of humidities of the air between
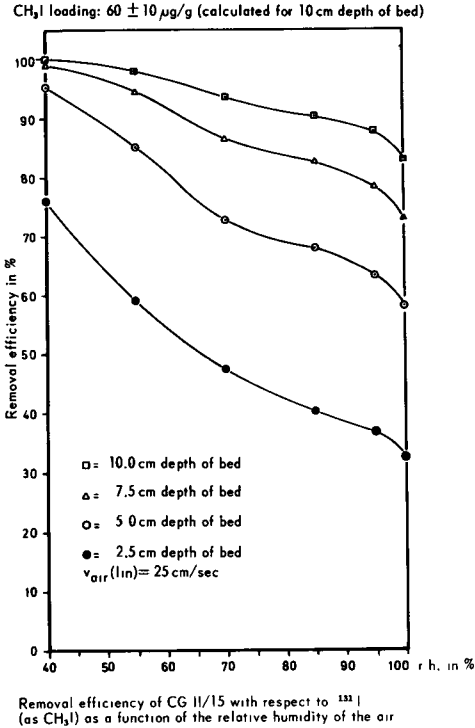40 and 100 % r.h. This experiment and all the following experiments

CH₃I loading: 60 ± 10 μg/g (calculated for 10 cm depth of bed)



Removal efficiency of CG II/15 with respect to $^{131}$I
(as CH₃I) as a function of the relative humidity of the air

**Fig. 6**

Test conditions:
Humid air, 30° C
Conditioning ≥ 20 h
Exposure to carrier gas and test medium: 1 h,
sweeping time (carrier gas only): 20 – 22 h
Penetration cumulated over length of
experiment

  o    2.5 cm depth of bed
  •    5.0 cm depth of bed
  x    7.5 cm depth of bed
  ▽    10.0 cm depth of bed

Penetration of Linde 13 X Ag by CH₃ $^{131}$I as a function of the relative
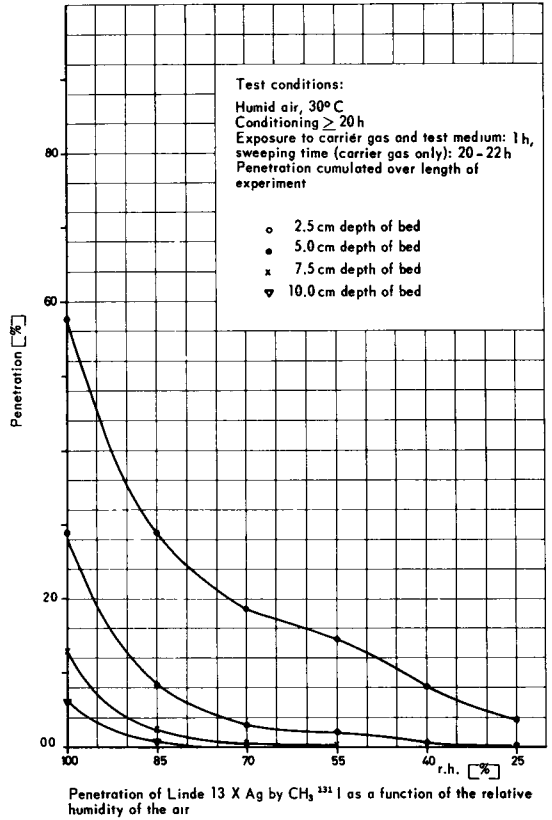humidity of the air

**Fig. 7**

were conducted on iodine sorption material which was in adsorption-
desorption equilibrium with the water vapor of the humid air stream.
While at 40 % r.h. of the air an activated charcoal bed of 10 cm depth
achieved a removal efficiency of 99.88 %, 98 – 100 % r.h. under other-
wise unchanged conditions gave rise to a removal efficiency of only
86 %. The increase in the humidity of the air raised the penetration
by a factor of 120.

Fig. 7 shows the penetration of LMS 13 X Ag by $^{131}$I in the form of
methyl iodide as a function of the relative humidity of the air in the
range between 25 and 100 % r.h. Again, there is an increase in penetra-
tion as the humidity of the air rises. At very high relative humidities
of the air, penetration will reach values so high that a limitation to
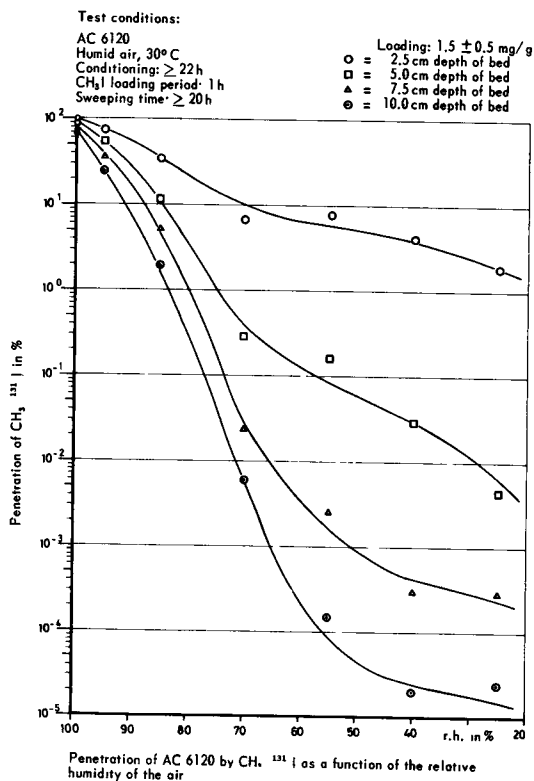70 % of the maximum relative humidity of the air seems to be preferable.

Test conditions:
AC 6120
Humid air, 30°C                                    Loading: 1.5 ±0.5 mg/g
Conditioning: ≥ 22h                          O = 2.5 cm depth of bed
CH₃I loading period· 1h                       □ = 5.0 cm depth of bed
Sweeping time· ≥ 20h                          ▲ = 7.5 cm depth of bed
                                             ⊘ = 10.0 cm depth of bed

Penetration of AC 6120 by CH₃ ¹³¹ i as a function of the relative
humidity of the air

Fig. 8

Fig. 8 is a diagram showing the results of studies on AC-6120 as the sorption material. The curves indicate a marked dependence of penetration upon the relative humidity of the air. Above approximately 70 % r.h., the penetration will increase so fast that again a limitation to 70 % of the maximum relative humidity of the air is probably useful.

At the end of this section it should be indicated that the relative humidity of the carrier gas and the related water vapor adsorption by the iodine sorption material under the operating conditions of most iodine filters used for gaseous effluent treatment are the most important parameters influencing removal efficiency.

## 8. Removal of Radioactive Iodine at High Temperatures of the Carrier Gas

High temperatures of the carrier gas may affect the iodine sorption material in the following way :

- Change the material and the impregnation so as to achieve lower removal efficiencies.

- Desorb iodine already removed.

- Ignite burnable sorption materials, such as activated charcoal.

The ignition temperature of activated charcoal varies greatly depending on a number of boundary conditions. Below 200° C ignition of activated charcoal in flowing air occurs relatively rarely. Desorption of iodine already removed may begin far below the ignition temperature (17,18). For this reason, the temperature limit for the use of activated charcoal must be fixed with respect to the desorption behaviour.
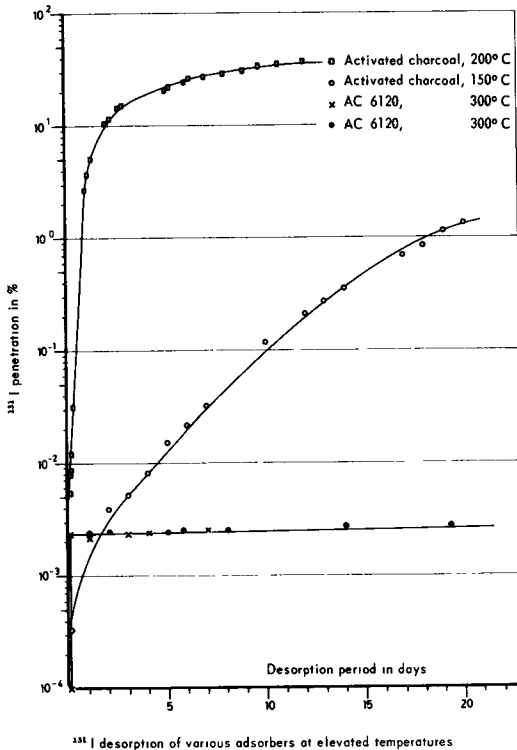
Fig. 9 shows the penetration of
10 cm deep beds of KI–impregnated
activated charcoal and AC–6120 at
elevated temperatures as a function
of time. At the beginning of the
experiment, the beds were exposed
to $^{131}$I in the form of methyl iodide.
The single dots in the curves indi-
cate the $^{131}$I activity in % penetra-
tion which had penetrated the test
beds, summed up until the respective
times of operation. Fig. 9 indicates
that with one of the usual KI–impre-
gnated types of activated charcoal
strong desorption occurs yet at
150° C. A value of 1 % penetration
is exceeded after 18 days at 150° C
and after only 24 hours at 200° C.
Both simple desorption of the iodine
adsorbed and oxidation of the acti-
vated charcoal and the iodine salts of the impregnation is assumed by
which, e.g., metal iodides are converted into elemental iodine which is
then desorbed, partly being transformed into more volatile iodine com-
pounds. The AC–6120 sorption material showed no major desorption while
exposed to air of 300° C over a sweeping time of 20 days. In
the light of the results available so far the iodine filter charcoal
mentioned here will be used in the Federal Republic of Germany only up
to temperatures of 120° C.

## 9. Removal of Fission Product Iodine of High Specific Activity

Usually laboratory experiments on iodine adsorption materials are
carried out only with very low activities (of the mCi order). In order
to prove the extrapolation to incident conditions in which high acti-
vity burdens will occur in the iodine sorption material, removal expe-

riments with high specific activities of the test agent $(CH_3{}^{131}I + CH_3{}^{127}I)$ were carried out in air at high humidity (98 – 100 % R.H.). Because of the high humidity, removal of the methyl iodide by adsorption was largely excluded. Accordingly, the test results give an indication of the effectiveness of the isotopic exchange process of iodine impregnated activated charcoal (19).



Penetration of activated charcoal beds by $^{131}I$ (introduced as $CH_3I$) when loaded with high activity levels
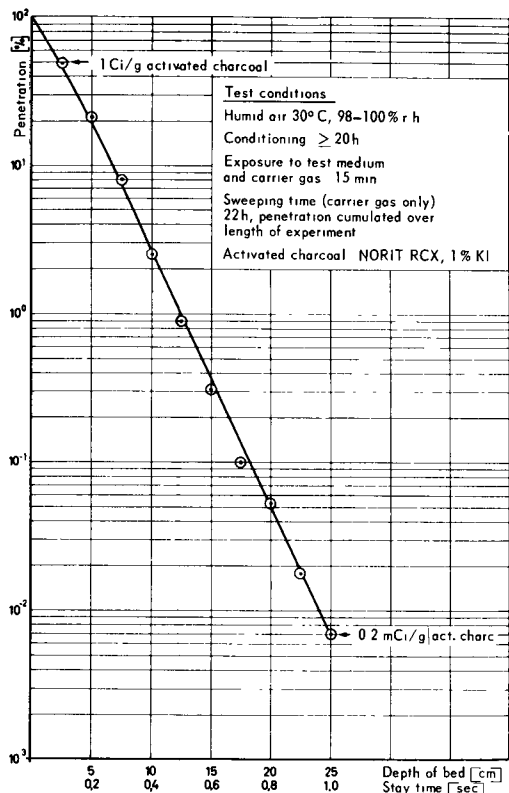
Fig. 10

Fig. 10 shows the penetration of ten successive test beds. Because of the removal of activity, the loading of the individual test beds decreases from 1 Ci/g of activated charcoal to 0.2 mCi/g. The curve indicates no influence of the different activity loadings upon the penetration of the individual beds. A comparison with additional experiments employing different activity loadings showed the same result.

If high iodine activities are removed, a high gamma dose rate in the sorption material must be expected to occur. In the presence of water the iodine removed by the activated charcoal can partly be transformed into organic iodine compounds which will be desorbed and in this way increase the penetration (20).

## 10. Removal of Fission Product Iodine at Minute Concentrations

A maximum release of $^{131}I$ from the stack of a nuclear power station during normal operation with a level of $\leqslant 0.1$ mCi/h corresponds to a concentration of fission product iodine in the exhaust air of $\leqslant 10^{-6}$ $\mu g/m^3$, if a volumetric flow of the exhaust air of 20,000 $m^3/h$ and a ratio of 1:20 between the quantities of $^{131}I$ and the other fission

product iodine isotopes is assumed. If this exhaust air concentration is achieved by a decontamination factor of the iodine filter of $10^2$, values $\leqslant 10^{-4}\ \mu g/m^3$ must be assumed for the concentration of fission product iodine in the untreated air, i.e., extremely low concentration levels which are even below the always present natural iodine content of the air (approximately $10^{-3}\ \mu g/cm^3$) (21).

Presently it is being discussed whether there is a concentration effect which will greatly reduce removal efficiencies in this low range of concentrations of fission product iodine.

Removal tests with successive filter beds adding up to large depths of bed indicate a reduction in removal efficiency of the individual beds as soon as a certain overall removal efficiency has been attained (see Fig. 5). It should be discussed whether this is a concentration effect as a consequence of which the removal of familiar forms of iodine, such as methyl iodide and elemental iodine, is generally no longer possible with sufficient efficiencies in the range of very low concentrations, or whether there is a partial conversion into compounds difficult to remove which remain after elemental iodine and methyl iodide have been filtered out and then determine the removal profile of the residual $^{131}$I activity. Studies carried out at our laboratory (22) indicate the following results (the concentrations given refer only to the added amount of radioactively marked iodine or methyl iodide; all experiments were performed in untreated air with the background of the natural iodine content) :

- It is not possible to indicate a fixed limit of concentration for the decrease in removal efficiencies to $I_2$ and methyl iodide.

- At very low concentrations ($\leqslant 10^{-6}\ \mu g/m^3$) methyl iodide exhibited the same removal behaviour as at higher concentrations (higher by a factor of $10^9$) (Fig. 11), if the methyl iodide had been adjusted to the desired concentration level by adding minute quantities to the carrier gas stream and not by means of pre-filtration.

- After removal of a large fraction of methyl iodide by filtration, a decrease of removal efficiency with increasing depths of bed will
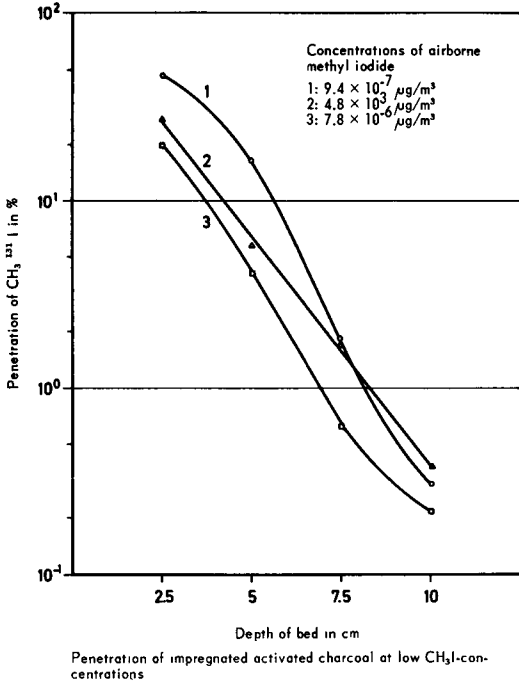
Penetration of impregnated activated charcoal at low CH₃I-concentrations

Fig. 11

occur also in higher ranges of concentration.

- Experiments using very low concentrations ($\leq 10^{-6}$ $\mu$g/m$^3$) of elemental iodine in the unfiltered air indicated a reduction in removal efficiency which from the bend in the steep initial slope of the removal profile can be explained by the existence of iodine compounds difficult to adsorb.

From these experimental findings it can only be concluded that the apparent dependence on concentration is simulated by the partial conversion of elemental iodine and methyl iodide, into compounds more difficult to remove or by the existence of volatile secondary products generated in the synthesis of $I_2$ and $CH_3I$, respectively, and which were not completely removed from the sample before introduction. Since the atmosphere is loaded with organic pollutants which may attain concentrations in the range of several mg/m$^3$, and since concentrations of fission product iodine were used which are lower by 9 orders of magnitude, a reaction of part of the more reactive elemental iodine with these compounds may be expected. There may also be reactions with airborne water vapor. Obviously, the properties of the iodine compounds produced by such conversion prevent an effective removal by adsorption and chemisorption. If they are sufficiently stable, it is not likely, for the same reason, that major fractions will be taken up by inhalation or by ingestion.

## 11. Ageing of Iodine Sorption Materials

The removal efficiency of iodine filters decreases with increasing ser-

vice life as a consequence of loading with pollutants which reduce the
effective surface of the sorption material by plating out or reacting
with the impregnation and the carrier substance, so as to generate un-
desirable products. In addition, there may be changes in impregnation,
e.g., as a consequence of crystal growth during storage, which may even
reduce the removal efficiency of iodine filters not in practical opera-
tion or of the replacement batches of sorption material.

The presence of filter pollutants in the gaseous effluents may prevent
the use of certain sorption materials. Activated charcoal, e.g., cannot
be used for filtering the $NO_2$-bearing gaseous effluent of a reprocessing
plant because it will quickly loose its removal efficiency in the $NO_2$-
bearing off-gases and, in addition, may react with the $NO_2$ violently
enough to ignite the activated charcoal.

The reduction in removal efficiency of the sorption material with time,
an effect produced by the accumulation of a number of processes, will
be summarized here under the generic term of "ageing". In the course of
this seminar, much will have to be said about this subject, especially
in connection with impregnated activated charcoal. Therefore, only a
few remarks will be made on the ageing of inorganic iodine sorption
materials which, however, can be extrapolated qualitatively to the
behaviour of iodine impregnated activated charcoal.

Fig. 12 shows the ageing behaviour of four successive filter beds made
of AC-6120, each having a depth of bed of 2.5 cm. The plot shows the
removal efficiency for $^{131}I$, which was introduced as methyl iodide, as
a function of the operating time and the number of air cycles, respecti-
vely (referred to the volume of the sorption material at 10 cm depth of
bed). The apparent linear air velocity during ageing and in the subse-
quent removal test was 25 cm/s. Air was continuously taken through the
filter beds from a reactor building; accordingly, the data may be re-
garded as being representative of a recycle air filter operating under
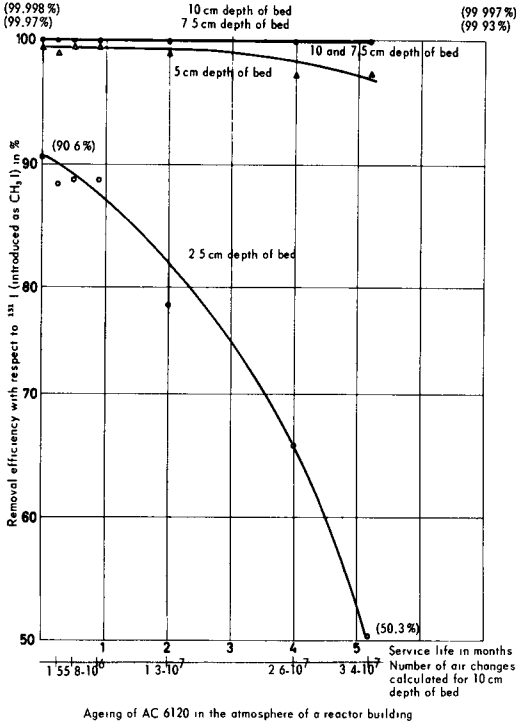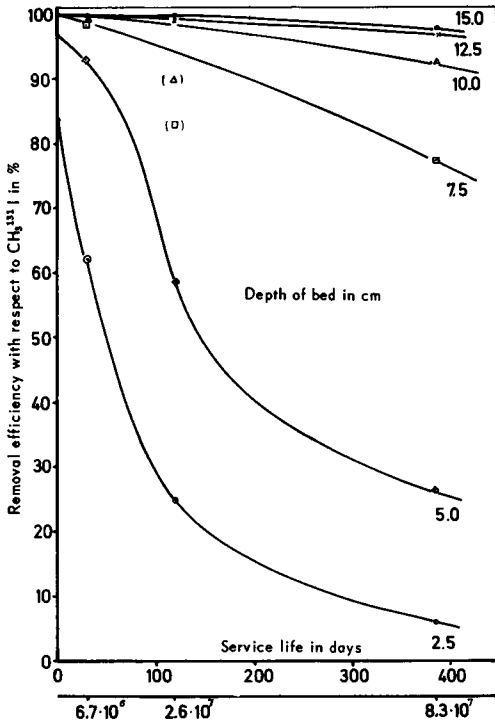the same conditions. The curves show that the overall removal efficiency

Ageing of AC 6120 in the atmosphere of a reactor building

Fig. 12

over four filter beds, corresponding to a depth of bed of 10 cm, after 5.2 months of continuous operation had decreased only slightly, from 99.998 to 99.997 %. However, in the first filter bed a marked decrease of removal efficiency from 90.6 to 50.3 % occurred over the same period of time. As was to be expected, these data indicate that ageing of the iodine sorption material occurred from the side of the unfiltered air. The differential removal efficiencies, i.e., the removal efficiencies of each filter bed evaluated separately (not entered in Fig. 12), already for the second filter bed, show no decrease of the removal efficiency over 5.2 months. The first filter bed had a good removal efficiency and high absorption capacity with respect to filter pollutants.

So it is recommended, in order to increase the permissible service life of a filter, to add a sufficient "ageing reserve" to the depth of bed of the iodine sorption material. In all the iodine sorption materials we have studied so far, increasing the depth of bed was capable of achieving an overproportionate extension of service life.

Fig. 13 shows the ageing of LMS 13 X Ag in industrial air at a future reactor site. In this case, ageing also extended to the second filter bed, which is indicated by a relatively steep slope of the overall removal efficiency over a depth of bed of 5 cm. Experiments conducted with additional beds placed upstream made of silver-free molecular sieves did not produce any better results.

Number of air changes calculated for 10 cm depth of bed
Ageing of LMS 13 X Ag in industrial air

Fig. 13

Finally, it can be said in the light of extensive ageing measurements performed on various types of iodine sorption materials that the use of flat filter beds, which are frequently designed without a sufficient reserve for the ageing factor is not meaningful and also completely insufficient as far as safety is concerned. The financial expenditure involved in frequent replacement and subsequent checking is in no way compatible with the savings in terms of iodine sorption material that can be achieved in a single filter unit.

Preliminary intercomparison studies showed that iodine impregnated activated charcoals had relatively short service lives and that it may be possible to extend the service life of iodine filters by means of triethylene diamine impregnated activated charcoal or inorganic iodine sorption materials impregnated with silver or silver salts.

The experiments on which the graphs shown in this paper are based were performed with equipment outlined in greater detail in the next paper, "The Testing of Iodine Filter Systems" *). The techniques of preparation and measurement will be covered by that same paper.

*) See Seminar vol. I, pp. 211-235.

## References

(1)  D.H.F. Atkins and A.E.J. Eggleton, Iodine Compounds Formed on
     Release of Carrier–Free Iodine–131, AERE–M–1211 (1963).

(2)  J.J. Hillary and J.G. Taylor, The Civil AGR Highly Active Gas
     Treatment Test, UKAEA, TRG Report 888(W)  (1965).

(3)  R.E. Adams, W.E. Browning, Jr, Wm. B. Cottrell, G.W. Parker,
     The Release and Adsorption of Methyl Iodide in the HFIR Maximum
     Credible Accident, USAEC–Report ORNL–TM–1291  (1965).

(4)  G.W. Parker, G.E. Creek, A. Ferreli, Retention of Methyl Iodide
     by Impregnated Carbons under Ambient Conditions, CONF–660904
     (1966), p. 199.

(5)  D.A. Collins, L.R. Taylor, R. Taylor, The Development of Impregnated
     Charcoals for Trapping Methyl Iodide at High Humidity, TRG 1300(W)
     (1967).

(6)  W.J. Maeck, D.T. Pence, J.H. Keller, A Highly Efficient Inorganic
     Adsorber for Airborne Iodine Species, CONF–680821 (1968), p. 185.

(7)  J.G. Wilhelm, Trapping of Fission Product Iodine with Silver–
     Impregnated Molecular Sieves, Actes du Congrès Saclay,
     4 – 6 Nov. (1969), p. 265.

(8)  J.G. Wilhelm, H. Schüttelkopf, Inorganic Adsorber Materials for
     Trapping of Fission Product Iodine, CONF–700816 (1970), p. 568.

(9)  J.G. Wilhelm, H. Schüttelkopf, An Inorganic Adsorber Material for
     Off–Gas Cleaning in Fuel Reprocessing Plants, CONF–720823 (1972),
     p. 540.

(10) Ch. Donner, T. Tamberg, Zur Abscheidung von Methyljodid und
     Aethyljodid an Silber–Zeolithen, Atomwirtschaft 16, 28 (1971).

(11) W.C. Schmidt, Treatment of Gaseous Effluents, TID–7534 (1957),
     p. 371.

(12) K.C. Patil, C.N.R. Rao, J.W. Lacksonen, C.E. Dryden, The Silver
     Nitrate-Iodine Reaction : Iodine Nitrate as the Reaction Intermediate,
     J. Inorg. Nucl. Chem. 29 (1967), p. 407.

(13) G.D. Parfitt, A.L. Smith, A.G. Walton, J. Phys. Chem. 69 (1965),
     p. 661.

(14) J.G. Wilhelm, H.G. Dillmann, K. Gerlach, H. Schüttelkopf,
     Jodfilterprogramm, in KFK 1565 (1971), p. 175.

(15) J.G. Wilhelm, Adsorbermaterialien zur Abscheidung von Spaltjod aus
     den Abgasen kerntechnischer Installationen, Reaktortagung 1970,
     Tagungsbericht, p. 339.

(16) D.T. Pence, F.A. Duce, W.J. Maeck, Developments in the Removal of
     Airborne Iodine Species with Metal-Substituted-Zeolites,
     CONF-720823 (1972), p. 417.

(17) J. Caron, J. Vandermeersch, A. Charmathieu, M.F. Thal, Piégeage de
     l'iode et de l'iodure de méthyle à température élevée,
     Actes du Congrès, Saclay (1969), p. 285.

(18) H. Schüttelkopf, J.G. Wilhelm, Jodfilterprogramm, in KFK 1365
     (1970), p. 110.

(19) J.G. Wilhelm, Testing of Iodine Filters for Nuclear Installations,
     IAEA Proceedings Series; Treatment of Airborne Radioactive Waste,
     Vienna 1968.

(20) A.G. Evans, Effect of Intense Gamma Radiation on Radioiodine
     Retention by Activated Carbon, CONF-720823 (1972) p. 401.

(21) C.E. Junge, Air Chemistry and Radioactivity, Academic Press,
     New York (1963).

(22) J.G. Wilhelm, H.G. Dillmann, J. Furrer, K. Gerlach, Filterprogramm,
     in KFK 1818 (1972), p. 93.