# Removal Efficiency of Silver Impregnated Filter Materials and Performance of IodineFilters in the Off-Gases of the Karlsruhe Reprocessing Plant WAK

F.J. Herrmann, B. Herrmann, V. Hoeflich, Ch. Beyer
Wiederaufarbeitungsanlage Karlsruhe

J. Furrer
Forschungszentrum Karlsruhe / Germany

## Abstract

An almost quantitative retention of iodine is required in reprocessing plants. For the iodine removal in the off-gas streams of a reprocessing plant various sorption materials had been tested under realistic conditions in the Karlsruhe reprocessing plant WAK in cooperation with the Karlsruhe research center FZK. The laboratory results achieved with different iodine sorption materials justified long time performance tests in the WAK Plant. Technical iodine filters and sorption materials for measurements of iodine had been tested from 1972 through 1992. This paper gives an overview over the most important results.

Extended laboratory, pilot plant, hot cell and plant experiences have been performed concerning the behavior and the distribution of iodine-129 in chemical processing plants (Henrich 1980, 1981, 1988, 1996, and Herrmann 1992). In a conventional reprocessing plant for power reactor fuel, the bulk of iodine-129 and iodine-127 is evolved into the dissolver off-gas. The remainder is dispersed over many aqueous, organic and gaseous process and waste streams of the plant.

Iodine filters with silver nitrate impregnated silica were installed in the dissolver off-gas of the Karlsruhe reprocessing plant WAK in 1975 and in two vessel vent systems in 1988. The aim of the Karlsruhe iodine research program was an almost quantitative evolution of the iodine during the dissolution process to remove as much iodine with the solid bed filters as possible. After shut down of the WAK plant in December 1990 the removal efficiency of the iodine filters at low iodine concentrations had been investigated during the following years.

## I. Introduction

In connection with iodine monitoring different methods for sampling iodine in the off-gas streams of the WAK plant were used.

Sampling with caustic scrubbers does not allow to catch the organic iodine. By this method in the off-gas of the Kalrsruhe reprocessing plant WAK only 15 % of the total measured iodine could be trapped. Parallel measurements with a discriminating sampling system for inorganic iodine confirmed that only 10 to 20 % of the total iodine in this vessel off-gas stream was inorganic (Herrmann 1990).

It is well known that sampling and filtering of iodine with charcoal allows to detect organic and inorganic iodine species only at low humidity of the off-gas. Numerous publications in the past years and the following considerations demonstrate some problems encountered utilizing charcoal as sorption material. Charcoal is the most exhaustively studied adsorbent for iodine. High removal efficiencies can be obtained with plain or impregnated charcoal for elemental iodine. However acid vapors, organic vapors, and moisture seriously affect the efficiency of impregnated charcoal. In either case the use of charcoal in off-gas systems containing more than 6 % nitrogen oxides is severely limited (Rodger 1969).

Results of laboratory experiences in the Karlsruhe research center (FZK) have demonstrated that during long-term measurements (about two months) the iodide impregnated charcoal looses most of the inactive iodide impregnation due to the oxidation of the iodide by the air. A break-through of active iodine cannot be excluded.

In the special case of the vessel off-gases of reprocessing plants which are currently saturated with water vapor from the scrubbing columns and kerosene from the solvent, sampling with charcoal is problematic. The influence of the humidity on the removal efficiency of iodine samplers is reported by many authors and quantified by H. Schüttelkopf. At a relative humidity of >90 % iodine sampling is not effective. If 90 % humidity in the off-gas has been overstepped once, the following measuring periods are distinctly influenced. It must be guaranteed that the measuring conditions have a security distance from the dew point of the gas to be measured (Schüttelkopf 1976).

Due to the problems of trapping iodine for measurements and removal of iodine in the off-gases of reprocessing plants, inorganic silver impregnated materials have been developed and were used as sampling and as filter materials in the off-gas streams of the WAK plant (Furrer 1979, Wilhelm 1976 and Herrmann 1995).

## II. Testing of Silver Impregnated Iodine Sorption Materials and Iodine Filters

To optimize iodine sorption materials manufactured with different carrier materials and different silver contents, after the preliminary tests in the Karlsruhe research center, the sorption materials had been tested in by-pass streams of the WAK dissolver off-gas and the WAK vessel ventilation system, see figure 1 (Test conditions: temperature 140 °C, residence time 0.4 s; bed depth 0.1 m; gas flow rate 0.7 $m^3/h$; linear gas velocity 0.24 m/s).

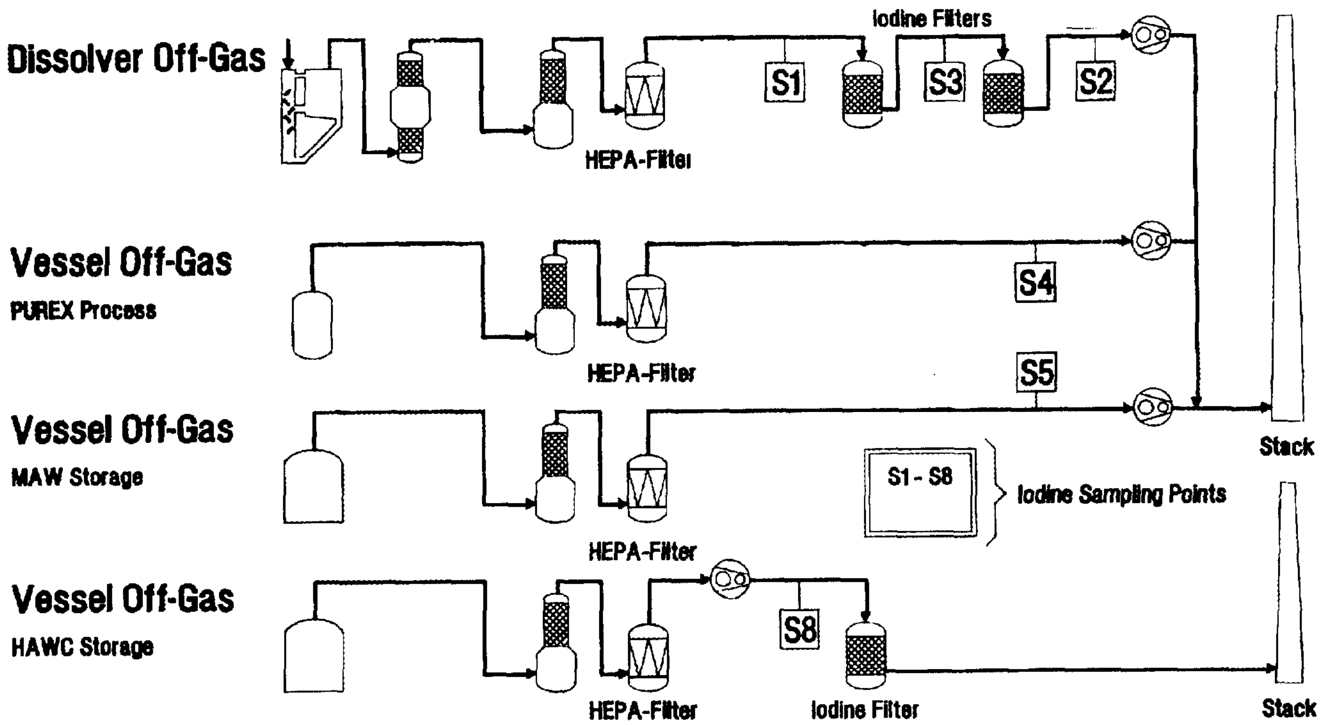


Figure 1 Offgas Cleaning of WAK with Iodine Filters and Iodine Sampling Points

For the investigations of the different sorption materials performed in the by-pass streams of the WAK dissolver off-gas (DOG) and the vessel off-gas (VOG), sampling points are located downstream the HEPA filters (upstream and downstream the iodine filters, see figure. 1). They allow to determine simultaneously the iodine concentration in the off-gas and the removal efficiency of the iodine filters). The gas stream is routed through absorption columns which are located in a heating cabinet. The internal diameter of the columns is 0.032 m. The gas flow rate through the columns is 500 l/h (STP). The column contains six successive beds consisting of the sorption material. Each bed is 0.05 m deep. The calculated residence time per bed is 0.2 s at 140°C. After different exposure times the columns were removed. The beds were emptied individually and the sorption materials were measured on a Intrinsic Germanium Planar Detector to determine its iodine-129 content.

## III. Evaluation of Silver Impregnated Iodine Sorption Materials

Experiments concerning the influence of the silver content of the carrier material on the iodine removal efficiency in the vessel off-gas of WAK have shown that an impregnation with 12 % silver is the optimum. Higher silver contents (for example 20 %) increase the risk of the efflorescence of the silver nitrate impregnation taking place in off-gases with 3 to 4 % of water vapor (resulting from the vapor pressure of the scrubbing columns working at 25 to 30 °C).

The essential parameters of sorption materials which may influence the removal efficiency of iodine sorption materials had been investigated. All materials had been impregnated with 12 % silver in form of silver nitrate. The porosity and the inner surface of the carrier material are decisive for the iodine removal efficiency. The alpha alumina shows a lower removal efficiency than the AC 6120.

The properties of the sorption material and the retained removal efficiencies are listened in table 1.

| Sorption material | AC6120 (Silica) | Alumina | Sinterglass |
|---|---|---|---|
| Grain size [mm] | 1 - 2 | 2 - 4 | 1 - 2 |
| Pore volume [ml/g] | 0.62 | 0.45 | 0.5 |
| BET surface [$m^2/g$] | 65 | 7 | 0.15 |
| Maximum of pore distribution [nm] | 20 - 40 | 75 | 10,000 - 40,000 |
| Silver content [%] | 12 | 12 | 12 |
| I-129 removal efficiency [%] | | | |
| - DOG of WAK | 99.8 | ----- | 90.0 |
| - VOG of WAK | 99.0 | 94.0 | 85.0 - 97.0 |

Table 1 Properties of sorption materials and iodine removal efficiencies in the off gas of WAK ( Bed depth 10 cm, residence time 0.4 s; DOG = dissolver off-gas; VOG = vessel off-gas)

In an earlier paper it has been shown that it doesn't matter whether the carrier material is silica or alumina. A silver impregnated gamma-$Al_2O_3$ (JFM 1) having a BET surface comparable to the BET surface of AC 6120, showed the same high removal efficiency as AC 6120 (Herrmann 1995). Besides temperature, residence time, silver content, iodine species and concentration in the off-gas,. the decisive parameters for iodine removal efficiency are the porosity and the BET surface.

## IV. Transferability of the Removal Iodine Efficiency Obtained by Small Scale Filters and Technical Filters

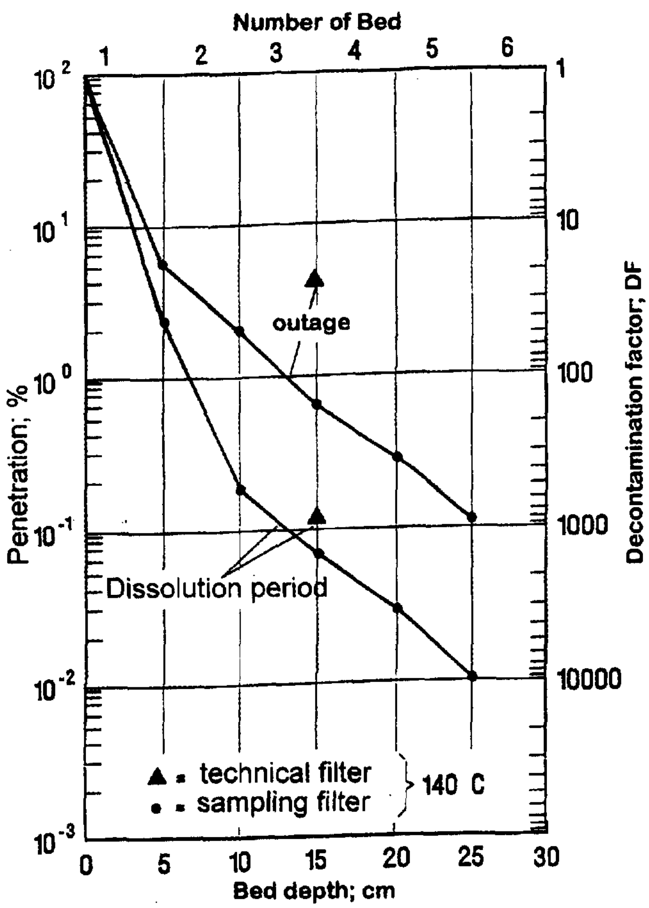


Figure 2 Removal efficiency of AC 6120 in a full size filter and in sampling filters.

The decontamination factors obtained with the small scale columns (sampling filter: inner diameter 0.032 m, bed depth 0.15 m) and the technical iodine filter (annular cylinder with a bed depth of 0.15 m), are traced in figure 2. The small scale filters reveal a higher iodine removal performance than the technical iodine filter. These values result from 12 measuring periods between 1989 and 1991.

The data for the iodine removal efficiency obtained by small sampling tubes (diameter 0,032 m, bed depth 0,1 m) are not directly transferable to the iodine removal performance obtained by full size iodine filters. Table 2 shows the iodine removal efficiency of a small size filter (bed depth 0,15 m, residence time 1.0 s, sorption material 0,078 kg) and a full size filter (annular cylindrical filter with a bed depth of 0.15 m and a filter diameter of 0.4 m, sorption material 35 kg).

| | Small size filter | Full size filter |
|---|---|---|
| Mass of AC6120/12 % Ag | 0.078 | 35 |
| Bed depth [m] | 0.15 | 0.15 |
| Temperature [°C] | 140 | entrance: 130, exit: 110 |
| Gas flow rate [$m^3$/h] | 0.5 | 80 to 120 |
| Linear velocity [m/s] | 0.25 | 0.15 |
| Residence time [s] | 0.6 | 1.0 |
| Iodine removal efficiency [%] | | |
| - during dissolution | 99.9-99.95 | 99.8-99.9 |
| - during outage | 98.7-99.3 | 94-96 |

Table 2 Comparison of iodine removal efficiency of a small scale and a full size iodine filter with AC6120/12% Ag in the dissolver off gas of WAK

The iodine removal efficiency of the full size filter is distinctly lower than the removal efficiency of the small size filters. The lower removal efficiency of the technical filter can be explained by channeling effects. The differences between laboratory scale filters and full size filters must be taken into consideration for the design of iodine filters in the off-gases of reprocessing plants.

## V. Performance of Iodine Filters in the Off-Gas Streams of the WAK Plant

### V.1 Dissolver Off-Gas

Two silver impregnated iodine filters in series were in operation in the dissolver off-gas of the WAK plant from 1975 through 1993. The filter material was a silver nitrate impregnated silica (AC 6120/12 % Ag). The filters worked at 110° to 130°C.

The dissolver off-gas filters were annular filters with the following characteristics:

| | |
|---|---|
| Outer diameter | 400 mm |
| Inner diameter | 106 mm |
| Thickness of annular section | 147 mm |
| Active filter volume | 54 1 |
| Number of filters | 2 filters in series |
| Sorption material | AC 6120, 35 kg per filter |
| Gas temperature | inlet 130 °C, outlet 110 °C |
| Dissolver off-gas flow rate | 80 to 120 $m^3/h$ |
| Residence time (off-gas) | 1.4 s |

The sorption material of the first filter was changed when the iodine removal efficiency of the first filter dropped significantly. Under normal operation conditions the iodine filters worked two years without interruption.

During dissolution periods the highest removal efficiencies of 99 to 99.9 % for the first iodine filter had been measured. The average iodine concentrations in the dissolver off-gas upstream of the iodine filter was in the range between 1 and 5 $mg/m^3$ obtained by discontinuous measurements. The peak values during dissolution were not measured because of the radiation power at the sampling points. They are in the order of 100 $mg/m^3$. During outage periods the removal efficiency of the first iodine filter was 97 %.

The removal efficiency of the second iodine filter was 90 % during dissolution period and 50 % during outage periods. The average decontamination factor of the second filter between 1989 and 1991 (two years of operation and one year after shutdown) was 4.

Downstream of the two iodine filters iodine-129 concentrations of about 0.005 $mg/m^3$ were observed during dissolution periods.

During the 15 years of operation a high stoichiometric loading up to 80 % of the first iodine filter had been achieved. The measured values of iodine loading were 17 GBq to 24 GBq. The corresponding service lives were 2 to 4 years for the iodine filter material.

**V.2 Vessel Ventilation System of the PUREX Process**

In 1987 a prototype iodine filter with a throughput of 35 $m^3/h$ and the following dimensions has been installed in a side stream of the vessel off-gas of the PUREX process:

| | |
|---|---|
| Diameter | 355 mm |
| Bed depth | 150 mm |
| Sorption material | 8.5 kg AC 6120 / 12 % Ag |
| Operating temperature | 140°C |
| Gas velocity | 14 cm/s |
| Residence time | 1 s |

The decontamination factor was determined by weekly measurements of the iodine concentration upstream and downstream the prototype iodine filter. The removal efficiency of the prototype filter in this off-gas stream was 90 to 95 %.

The decontamination factors are influenced by the iodine concentrations and by the nature of the iodine species present in the vessel off-gas. Iodine loading after 2.5 years of operation was 21.4 MBq (3.27 g of iodine-129) for the total filter. This corresponds to a stoichiometric loading of 0.33 %.

**V.3 Vessel Ventilation System of the Liquid High Active Waste Storage**

Up to now the iodine filter with AC6120/12 % Ag in the vessel vent system of the liquid high active waste storage is operating at about 40 °C and a gas flow rate of 180 $m^3/h$ up to now. An iodine removal efficiency of 90 % to 94 % is attained.

**Literature**

Furrer, J. 1979. Verfahrensentwicklung und Optimierung der Filter zur Auflöserabgas- reinigung. Report KfK 2750.

Henrich, E. and R. Hüfner. 1980 . Improved Procedures for Efficient Iodine Removal from Fuel Solutions in Reprocessing Plants, IAEA-SM-245/16.

Henrich, E., W. Roesch , F.Weirich. 1981. Improved Iodine and Tritium Control in Reprocessing Plants.16th DOE Nuclear Air Cleaning Conference, San Diego, 1980 (Conf-801038), 1981.

Henrich, E., R. Grimm, L. Finsterwalder. 1988. Ioddesorption aus der Brennstofflösung, ein Vergleich von Theorie und Experiment. Report KfK 4476 pp.155-200 (1988).

Henrich, E.1996. Control of Volatile Radionuclides in Reprocessing.
To be published in Kerntechnik, 1996.

Herrmann, F. J., V. Motoi, B. Herrmann, A. van Schoor, D. Fang, H. Fies. 1990. Retention and Measurement of Iodine-129 and of Organoiodine in the Off-gas Streams of the Karlsruhe Reprocessing Plant WAK. 21st DOE/NRC Nuclear Air Cleaning Conference, San Diego 1990, CONF-900813. pp 222-233.

Herrmann, F.J., R. Grziwa, L. Finsterwalder, D. Fang, B. Herrmann, V. Motoi, Ch. Beyer.1992. Iodverteilung in einer Wiederaufarbeitungsanlage am Beispiel der WAK.
Annual Meeting on Nuclear Technology-Jahrestagung Kerntechnik 5.-7. Mai 1992, Karlsruhe Proceedings 0720-9207.

Herrmann F.J., V.Motoi, B. Herrmann, D. Fang, L. Finsterwalder, K.D. Kuhn, A. van Schoor, Ch. Beyer, J. Furrer, W. Knoch. 1992. Minimizing of Iodine-129 Release at the Karlsruhe Reprocessing Plant WAK. 22st DOE/NRC Nuclear Air Cleaning Conference, Denver 1992.

Herrmann, F.J., B. Herrmann, D. Fang, M. Weishaupt, J. Furrer, T. Engelhardt. 1995.
15 Jahre Erfahrungen mit Iodfiltern im Abgas der Wiederaufarbeitungs- anlage Karlsruhe WAK. Annual Meeting on Nuclear Technology, Nürnberg, 16. - 18. Mai 1995.

Rodger, W.A. and S. L. Reese. 1969. The Removal of Iodine from Reprocessing Plants Effluents. Reactor and Fuel-Processing Technologiy, Vol. 12, No. 2, pp. 173-180, 1969.

Schüttelkopf, H. and H. Fessler. 1976. Die Messung von Iod-131 in der Umgebungsluft kerntechnischer Anlagen. Report KFK 2350.

Wilhelm, J., J. Furrer, E. Schultes. 1976. Head End Iodine Removal from a Reprocessing Plant with a Solid Sorbent. 14th DOE Air Cleaning Conference, Idaho Falls.

## DISCUSSION

**JUBIN:** A point of clarification concerning the difference between your technical filter and your sampling filter, you indicated that the sampling filter always had better performance than the technical filter. Was the technical filter exposed to other contaminants for a longer period of time than the sampling filter? The question is, did they have the same history? Can this be attributed to the length of time the sampling filters were in service or to other contaminants?

**HERRMANN:** The technical filter has always had distinctly lower removal efficiency than the sampling filter, even for the same experimental conditions and exposure times. Experiments performed with sampling filters of different sizes (diameter 25mm and 33mm) showed the same phenomena. The smaller the filter diameter, the better the removal efficiency. When sampling filters and technical filters had the same service life, the sampling filters always showed a better iodine removal efficiency.

**SAKURAI:** You use the two DOG filters in series at the WAK reprocessing plant. Why is the DF lower for the second filter than for the first one? Is it a commonly observed phenomenon?

**HERRMANN:** This has commonly been observed. The iodine concentration entering the second filter is by 3 orders of magnitude lower than the iodine concentration entering the first filter. The iodine species are probably different.