

MERCURY PURIFICATION IN THE MEGAWATT LIQUID METAL SPALLATION TARGET OF EURISOL-DS

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High power spallation targets are going to be used extensively in future research and technical facilities such as spallation neutron sources, neutrino factories, radioactive beam facilities or accelerator driven systems for the transmutation of long-lived nuclear waste. Within EURISOL-DS, a 4 MW liquid metal spallation target is designed to provide neutrons for a fission target, where neutron rich radionuclides will be produced. For the spallation target, mercury is planned to be used as target material. A large amount of radionuclides ranging from atomic number Z=1 to 81 will be produced in the liquid metal during long term irradiation. It is planned to remove those radionuclides by chemical or physicochemical methods to reduce its radioactivity. For the development of a purification procedure, knowledge about the chemical state of the different elements present in the mixture is required. We present a general concept of applicable separation techniques in a target system and show some results of experiments on the chemical behavior of radionuclides produced by proton irradiation of mercury as well as the first successful separation experiments.

I. THE MULTI-MW MERCURY SPALLATION TARGET OF EURISOL-DS

EURISOL-DS¹ is a study aiming for the design of a next-generation ISOL (Isotope Separation On-Line)² facility that should provide the scientific community with radioactive ion beams (RIB) of hitherto unprecedented intensity and quality. For the generation of RIBs of short-lived exotic neutron rich nuclides that are of great interest e.g. with respect to fundamental nuclear physics questions, it is planned to develop a fission target where these nuclides are produced by neutron induced fission reactions. The neutrons will be provided by a liquid metal spallation target with a 4 MW proton beam interacting with mercury. To reduce the radioactive inventory of the target material, it is planned to purify the mercury by chemical or physicochemical methods.

II. LIQUID METAL TARGETS FROM A CHEMIST'S POINT OF VIEW

From a physicochemical point of view, a liquid metal spallation target is an extremely complex heterogeneous multi-component system, comprising macroscopic phases such as construction materials, the liquid metal and the cover gas plenum, as well as many micro-components. The latter can be present in different concentrations and chemical states, depending on operating conditions such as temperature, pressure, liquid metal flow, redox potential and proton dose. These micro-components are of different origin:

Gaseous impurities include oxygen, nitrogen and water. The construction materials contribute oxides, nitrides and carbides, apart from their main components and alloying elements. Furthermore, in a target using mercury as target material, all elements from the periodic table ranging from atomic number 1 (hydrogen) up to 81 (thallium) will be produced in considerable amounts by nuclear reactions such as spallation, fission, fragmentation and activation. These elements can undergo chemical reactions with the macro-components and among each other.

A continuous transport of material is caused by the flow of the liquid metal as well as gradients in temperature and chemical potential, where mobilization, transport and deposition processes can occur in the system. Here, mobilization processes are mainly dissolution processes such as corrosion. Additionally, the fast flowing liquid metal can cause erosion of the construction materials. This effect can be greatly enhanced by the presence of hard solid particles suspended in the liquid that can be formed by precipitation of insoluble phases as well as by breaking-off crystallites from the construction materials in corrosion processes. Furthermore, gas phase transport processes involving gaseous or volatile species can occur. Surface properties of the construction materials may be altered by diffusion processes, where materials can be transported from the construction materials to the liquid phase or in opposite direction, i.e. from the liquid to

surface layers and/or the bulk solid phase. These diffusion processes are enhanced by the strong radiation field, especially in vicinity of the target window, but also to a lesser extent in the complete target system.

Precipitation processes can include formation of local coatings as well as formation of mobile insoluble particles. As a consequence of the chemical complexity of the system, the nature of precipitations is expected to be equally complex. In principle, formation of metallic or intermetallic platings on metal surfaces have to be considered as well as precipitation of particles of intermetallic phases, oxides, salts, nitrides or hydrides. These materials, depending on their wetting properties, their density difference compared to the liquid metal and their particle size, can remain suspended in the liquid or accumulate e.g. at the liquid/gas interface, at the walls of the target or liquid metal loop or sediment at the bottom at positions with low flow rate or during maintenance periods when the liquid metal flow is stopped.

Taken as a whole, transport processes cause a continuous chemical stress for the integrity of the complete liquid metal target and loop system. This also includes the degradation of passivating surface layers and embrittlement of construction materials caused by dissolution or incorporation certain components. The presence of halogens and chalcogens produced by nuclear reactions can have catalysing effects on degradation and corrosion processes. The hydrogen-water vapour pressure ratio, which is determining the reductive potential, is one parameter that is decisive for the chemical state of different components. This ratio is not known a priori, nor is it constant within the operation period of the target unless special measures such as integration of an oxygen control system are taken.

Overall, an inhomogeneous distribution of nuclear reaction products has to be expected for a liquid metal target system. The implications for operation and maintenance of the systems are numerous: The formation of surface layers throughout the complete target and loop system and the distribution of radionuclides between surfaces and bulk mercury are largely dependent on the operating conditions. At the start-up, the concentration of nuclear reaction and corrosion products is very small. Therefore, homogeneous surface layers cannot be formed. On the other hand, because of the high ratio of adsorption sites on surfaces compared to the number of impurity atoms present at an early stage of operation, it is likely that a substantial fraction of the radionuclides produced are adsorbed at the surfaces. With increasing irradiation time the concentrations of nuclear reaction and corrosion products will get larger and larger. This can lead to an overall increasing ratio of radionuclides carried with the liquid metal, compared to the adsorbed material. Additionally, coatings could be formed, preferably at special positions such as the heat exchanger, where low solubility compounds could precipitate at the relatively

low temperatures present. This could lead to changes in heat conduction, resulting in a change of performance of the heat exchanger. In general, an inhomogeneous distribution of decay heat and radiation has to be taken into account. This has consequences e.g. for shielding calculations or maintenance operations at different components. Furthermore, the accumulation of nuclear reaction products at the liquid/gas interface may lead to enhanced evaporation of volatiles caused by decay heat.

II.A. The Chemical State of Nuclear Reaction Products in a Liquid Mercury Target

Apart from its function as target material and heat transfer medium, mercury in a liquid metal spallation target acts as a solvent and reaction medium for nuclear reaction and corrosion products. Initially, nuclear reaction products will be present in the target in atomically dispersed form until reaching a certain saturation concentration, unless they react with another chemical species to form a compound or attach to a surface providing suitable adsorption sites. Such surfaces may be provided by the construction materials, by impurity particles suspended in the liquid metal or solid impurities accumulated at phase boundaries such as the liquid gas interface. For an element that does not undergo chemical reaction or adsorption processes, its saturation concentration is determined by its solubility. In case chemical reactions occur, the solubility of the resulting compound in mercury determines the state of the element under consideration within the system. The solubility of many compounds in mercury may be very low, e.g. metal oxides. The solvent mercury, which is present in a large excess, has to be considered to be a principal reaction partner for nuclear reaction products. However, there are compounds that are much more stable than the corresponding compounds of nuclear reaction products with mercury. Consequently, mercury can be displaced from the primary chemical reaction products by other impurities. Therefore, it is expected that finally various other compounds are formed from all the elements present, leading to a minimization of the Gibbs free energy of the system. With increasing irradiation time, reactions of nuclear reaction products among each other become more probable because of the higher concentrations.

From the situation described above, it is concluded that the solubility of elements and compounds play a major role in the understanding of nuclear reaction product behaviour in mercury. A discussion of solubility data available in the literature and a semi-empirical method for the estimation of missing data can be found in Ref. 3.

Furthermore, the interaction of nuclear reaction products with the liquid metal and among themselves will

have a decisive influence on their chemical state within the target system. In principle, the chemical state of different components can be evaluated based on thermodynamic data, e.g. using the method of Gibbs free energy minimization. However, this requires a complete and consistent set of thermodynamic data for all possible species/phases that could be present in the system. For a system comprised of elements from almost the complete periodic table such as a mercury target, i.e. a system comprising more than 80 components, this is definitely unrealistic, since even for binary combinations some data are lacking. In such a complex system the formation of ternary, quaternary and more complex phases can be expected. Even the formation of hitherto unknown phases is possible. Therefore, a complete and consistent data set comprising all possible phase and species is out of reach. In a much simplified approach, the general behaviour of the different elements formed by nuclear processes in a liquid metal spallation target could be estimated based on an evaluation of the strength of chemical interaction in binary combinations of elements. The viability of this approach is under investigation in our group.

III. EXPERIMENTAL MODEL STUDIES ON PROTON IRRADIATED MERCURY SAMPLES

III.A. The Distribution of Radionuclides in Proton Irradiated Mercury Samples

Two 1 ml samples of Hg were filled in stainless steel capsules. These capsules were irradiated at CERN with a proton beam of 1.5×10^{15} protons of 1.4 GeV. After some weeks of cooling the samples were transferred to PSI, where they were measured on an HPGe-detector equipped with standard electronics. One sample (Sample 1) was opened in a Plexiglas glove box, which was filled with Ar. The Oxygen content of the system measured using an yttria-doped ZrO_2 solid electrolyte cell was in the range of 0.1 – 1 %. After opening, the Hg was removed from the steel capsule and poured into a glass vessel. γ -spectra of the steel capsule and the complete Hg sample were taken. Additionally, a part of the bulk Hg, inside the droplet, was separated using a syringe, and a γ -spectrum of the removed fraction of Hg was measured. The second sample (Sample 2) of Hg remained in the original irradiation capsule. γ -spectra were taken repeatedly to facilitate nuclide identification based on decay properties.

Fig. 1 shows a small section γ -spectrum of Sample 1 approximately 6 weeks after irradiation, clarifying the complexity of the spectrum. With the aid of spectra of both samples taken in the following months, various nuclides of the elements Ag, Ba, Ce, Gd, Eu, Lu, Hf, Re, Os, Ir, Pt, Au, Hg and Tl have been surely identified. For some isotopes of Se, Rb, Y, Zr, Nb, Mo, Ru, Sn and Yb the identification is less certain.

A comparison of the γ -spectra of the mercury removed from the irradiation capsule and the capsule itself indicates that a substantial part of the activity is retained on the surface of the capsule, but a large part of the activity is carried away with the liquid metal as well.

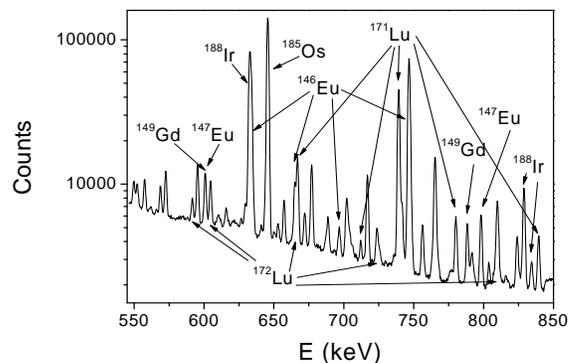


Fig. 1: Section of the γ -spectrum of sample 1 taken approximately 6 weeks after irradiation.

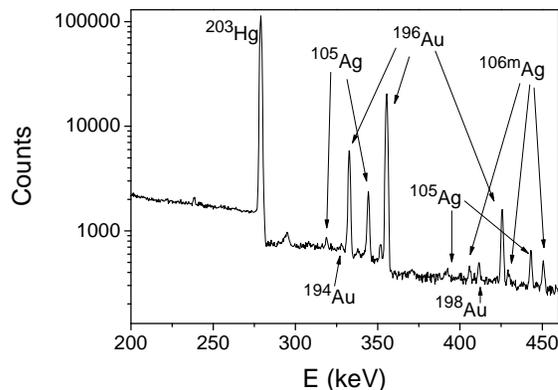


Fig. 2: Section of the γ -spectrum of bulk Hg removed from sample 1 using a syringe, taken approximately 6 weeks after irradiation

The γ -spectrum of the fraction of Hg separated using a syringe showed much less activity than expected from the spectra of the complete mercury removed from the capsule. In fact, only silver and gold isotopes could be identified in this sample (see Fig. 2). Since this sample was taken from the inner part of the Hg droplet, it is concluded that only Ag and Au are actually dissolved in mercury, while the radionuclides of the remaining elements are attached to the surface of the Hg droplet. These nuclides are also those that are preferentially adsorbed at the surface of the irradiation capsule. In comparison, Ag and Au are completely removed from the irradiation capsule together with the mercury. No Ag and Au nuclides were found in the γ -spectrum of the irradiation capsule after emptying the Hg.

The reason for this behavior and the chemical state of the radionuclides located at the surfaces is not yet fully understood. However, it is known from aqueous

radiochemistry that radionuclides present in carrier-free amounts often undergo adsorption processes, either on the walls of containers or on solid particles dispersed in the system⁴. A rough comparison of the number of adsorption sites available in the capsule with an estimation of the total number of atoms produced during irradiation shows that substantial adsorption of radionuclides at the walls of the capsule is possible. A quantitative comparison of the γ -spectra of capsule surface and both complete and inner part of the Hg sample is difficult because of the strong absorption effect of Hg and non-sufficient knowledge of the actual distribution of the γ -emitting species.

Though the surface of the Hg samples was visually clean, a thin layer of solid material, e.g. oxide, could be present on the surface of the liquid metal. Since this material would be finely dispersed, it can serve as a site for adsorption of carrier free radionuclides. Therefore, adsorption to such particles could be an explanation for most of the radionuclides being enriched on the surface of the liquid metal. Other possible explanations are segregation of metals because of low solubility, oxide formation due to reactions with impurity oxygen or with oxide layers present in the capsule. These reactions may be enhanced by radiation. Segregation due to solubility limits seems to be a plausible explanation for the least soluble elements. For instance, for the element Re solubilities in the range of mole fractions of 10^{-15} have been predicted by semi-empirical calculations³, while from the γ -spectrum of our Hg sample we estimate a mole fraction of 10^{-11} for the isotope ^{183}Re . In general, the presence of inactive carrier can play an important role in solubility considerations. Though radionuclides are present only at low concentrations in our samples, typically mole fractions of 10^{-11} to 10^{-14} , corresponding inactive carriers can be present in much larger concentrations. In this way, the solubility limit can be exceeded. The formation of oxides is the most probable explanation for the separation of those elements that have a high affinity to oxygen.

For a liquid metal spallation target, several consequences of these effects have to be considered. For example, shielding calculations are performed assuming a homogeneous distribution of radionuclides in the target. A deposition of radionuclides on the walls of the loop could lead to higher than expected dose rates. Additionally, the radioactivity is not necessarily carried away with the liquid metal but partially remains in the loop after emptying the loop for maintenance operations. Furthermore, the deposition effect would influence the techniques that can be used for purification. It would be highly desirable to investigate such effects in a real Hg spallation target and loop, e.g. at SNS at ORNL.

III.B. Experimental Studies on the Removal of Radionuclides from Mercury

A sample of approximately 2 g Hg was proton irradiated at CERN. After cooling for several years under ambient conditions in contact with air, the sample was sent to PSI. γ -spectroscopy showed that the main activity remaining in the sample stems from long-lived isotopes such as ^{173}Lu , ^{172}Hf and its daughter ^{172}Lu as well as ^{194}Au as a daughter of ^{194}Hg . Visually, the sample did not show the bright metallic luster displayed by pure mercury. Its surface had a rather dull grey appearance, indicating the presence of a thin oxide layer. A part of the mercury was separated from the bulk sample using a syringe in such a way that only material from the inner part of the Hg droplet was separated. The γ -spectrum of this fraction of Hg showed only the peaks of ^{194}Au , indicating that the Lu and Hf nuclides are attached to the surface of the sample rather than dissolved in Hg. This is consistent with the distribution of radionuclides observed in the other two samples mentioned before. Those of course contained many more radionuclides because of the more recent irradiation. Presumably, Lu and Hf are oxidized, since they are metals that are rather sensitive to oxidation. Since a spallation target system is not an ultra-pure environment, oxidation processes can be expected to occur in such a system as well. Therefore, the formation of oxide material may occur in a target system, and methods to remove these can be an efficient way to remove a part of the radionuclides formed by nuclear reactions. The removal of this material should also help to prevent the deposition of solid materials at unwanted places, e.g. plugging of thin pipes.

To separate the surface layer from the liquid metal, the mercury droplet was brought into contact with oxidic materials having a rather rough surface. For the first experiments, the Hg droplet was moved in boats made of chinaware and sintered corundum. For the final experiment, the sample was poured over molecular sieve. Fig. 3 shows the γ -spectra of the sample before and after pouring over the molecular sieve. The Lu and Hf nuclides are almost quantitatively removed from the mercury, whereas the gold remains in solution. The Hg sample also showed bright metallic luster after the cleaning procedure.

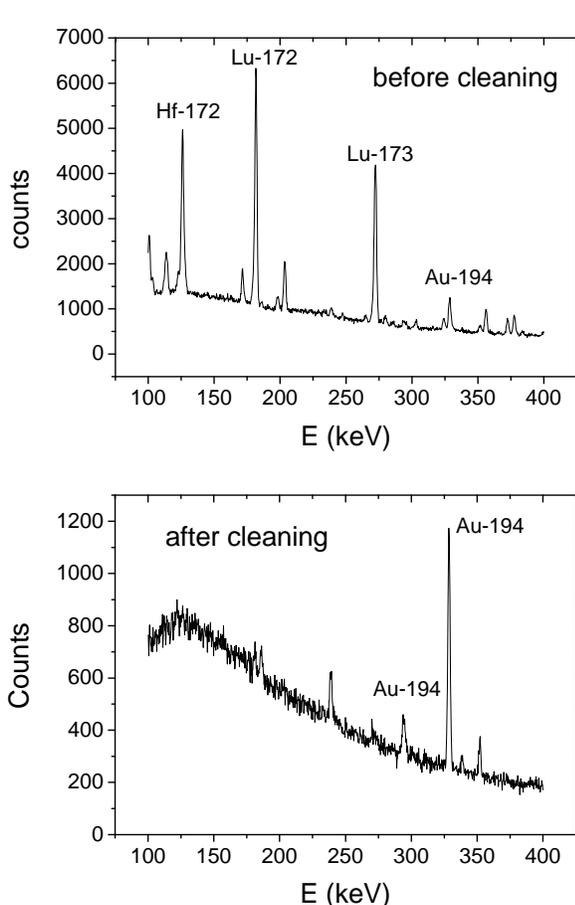


Fig. 3: γ -spectra of the Hg sample before and after pouring over molecular sieve.

Further experiments were carried out to find methods for removal of dissolved components, in this case ^{194}Au . For these experiments, the Hg sample remaining from the Lu/Hf-separation was used. ^{194}Au as the major radioactive component detectable by γ -spectroscopy is produced from its mother ^{194}Hg with a half-life of 520 y. From an evaluation of intermetallic interactions based on semi-empirical calculations⁵, metals of Group 4 and 5 of the periodic table should have a higher affinity to gold than mercury. Furthermore, these metals are hardly soluble in mercury. Therefore, they should be suitable candidates for absorbers. In the first experiments, Ta and Zr foils were brought into contact with mercury, but no wetting of the metal surface could be achieved. Several methods of surface treatment have been examined to facilitate wetting of the metal surfaces, e.g. mechanical scratching, etching and treatment with complexing agents. Since none of them was successful, other candidates for metal absorbers had to be found. Copper seemed attractive since it is well known to form compounds with gold, and its solubility in mercury is fairly low. Furthermore, copper can be amalgamated fairly easily. Therefore, wetting of copper with mercury should be

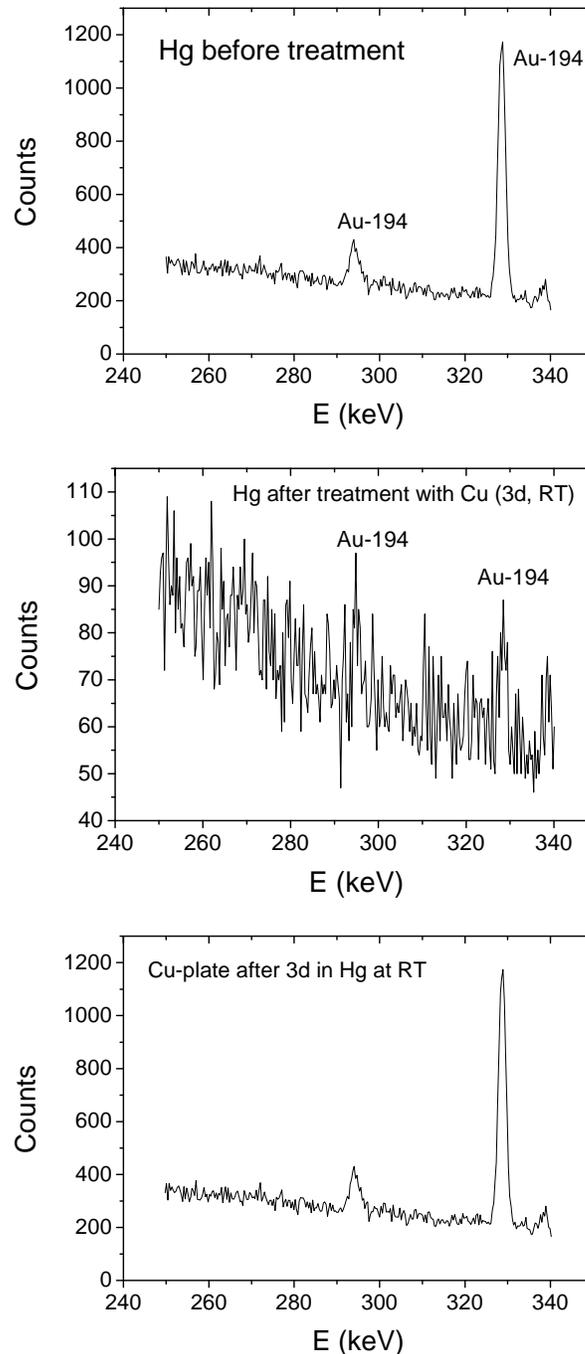


Fig. 4: γ -spectra of the Hg sample before and the Hg sample and Cu-plate after the adsorption experiment.

possible. In practice, wetting of copper is slow and incomplete when dipping a mechanically cleaned copper plate into mercury. The wetting can be enhanced by amalgamation of the copper plate. For this purpose, the copper plate is dipped in a saturated aqueous HgCl_2 -solution for several hours. After this procedure, a Cu-amalgam layer has formed at the surface of the plate.

After removal of precipitated CuCl the surface shows a silvery metallic luster.

The amalgamated Cu-plate was placed in the gold-containing mercury sample for three days under ambient conditions. γ -spectra of the mercury sample were taken before and after the experiment. The Cu-plate was measured on the γ -detector as well, after the experiment.

The results of γ -spectrometry are shown in Fig. 4. After the treatment, Au is almost quantitatively removed from Hg and attached to the Cu-Plate. The kinetics of the process is now under study. First results indicate that the process is quite fast, i.e. about 50 % of the gold is adsorbed within 15 min.

The results obtained suggest that metal absorbers could indeed be used to remove dissolved nuclear reaction products from a spallation target system. However, it is unclear if this method only works for carrier free amounts as present in the experiments described here. In a high power spallation system the final concentrations of dissolved components could be much higher and the absorber surface could be saturated. Therefore, the capacity of such a metal absorber has to be determined and in practice probably it has to be replaced from time to time when an efficient removal of dissolved components is desired. Other candidates that could be removed from Hg using a Cu-absorber would be e.g. Zn and Sn. These metals are soluble in Hg, and are known to form stable phases with Cu. These systems will be studied in our laboratory.

IV. A CONCEPT FOR MERCURY PURIFICATION IN A SPALLATION TARGET LOOP

In principle, the impurities present in a spallation loop can be divided in different classes according to their physical and chemical state. First of all, one has to deal with gaseous nuclear reaction products, predominantly hydrogen, helium and the heavier noble gases. Non volatile elements can be divided in two classes: highly and less soluble. Many elements produced by nuclear reactions will undergo chemical reactions and form solid compounds, e.g. oxides or intermetallic phases, which have a low solubility in Hg. These compounds, according to their density, will tend to either float on top of the liquid metal, to sediment or to form particles dispersed in the liquid metal.

Gaseous impurities will diffuse out of the liquid metal fairly fast at the liquid-gas interface that will be present in an expansion tank within the loop. If necessary, the heavier, condensable noble gases could be retained in cooled zeolite traps. For hydrogen, catalytic conversion to water and gettering of the latter on a drying agent has been discussed for MEGAPIE, but this approach was not realized and model studies are still pending.

For removal of dissolved components, metal absorbers could be useful, as demonstrated by the above mentioned example showing the removal of Au from Hg with a copper plate.

Since the solubility usually decreases with decreasing temperature, less soluble species can be precipitated at a cold trap. For solid phases floating on top of the liquid gas interface, we suggest a skimming procedure, while particles carried with the liquid metal stream could be filtered out using filters made of high surface area material, as demonstrated above for the separation of Lu and Hf from mercury. These filters probably would have to be placed in a bypass to avoid serious consequences for the flow conditions in the main loop. Should phases with higher density than mercury be formed, they will generally tend to accumulate in the lower part of the loop. In case there are unfavorable flow conditions, these materials might accumulate at certain positions and influence the operation of the loop. In case they don't sediment but are carried by mercury, they will be either trapped by the suggested filter systems or finally sediment in the storage tank where Hg is stored during maintenance.

In general, to efficiently avoid a contamination of the loop we recommend integrating the suggested devices as close as possible to the region where the impurities are produced, i.e. directly behind the spallation target. Of course, these procedures are still not in a mature state and need much more basic research, technical development of the separation devices and finally integration in the target loop

Other possible methods for purifying mercury include distillation or treatment of Hg with oxidizing agents (e.g. oxygen or aqueous HNO_3) and removal of the oxidized impurities. Distillation would have to be carried out offline. From radioprotection considerations the evaporation of many tons of highly radioactive Hg seems undesirable. Furthermore, even if it is technically feasible, it remains questionable if this technique would be economically favorable. Oxidation with oxygen and skimming of the oxidation products could be feasible online. However, this procedure might induce larger amounts of solid oxide material that could harm the operation of the loop. The extraction of impurities using aqueous oxidizing agents will produce a large amount of liquid radioactive waste. This has disadvantages for disposal, but may be advantageous if one wants to extract carrier-free radionuclides for certain applications. The online methods using cold traps, filters, skimming and metal absorbers on the other hand don't produce additional liquid radioactivity. Furthermore, due to their chemical diversity, they will provide a certain chemical selectivity that could be very helpful if some of the extracted radionuclides are to be exploited for medical or technical applications.

Offline methods in general have a disadvantage: They will not protect the loop from contamination. Application of the online methods suggested above, such as cold trap, skimming of expansion tank, metal absorbers and filters opens the possibility to continuously reduce the radioactive inventory and thus contamination of the loop during operation. However, the efficiency of the suggested devices cannot be judged at the present state. Another advantage of online methods is that they could provide access to nuclides with shorter half-life that may be of medical and technological interest. For this purpose, suitable remote handling techniques to replace the separation devices and appropriate chemical separation procedures would have to be developed.

V. CONCLUSIONS

In this paper, we discuss the chemical behavior that can be expected for nuclear reaction and corrosion products in a liquid metal spallation target loop. In general, an inhomogeneous distribution of these impurities in the loop can be expected due to dissolution and deposition processes and physical and chemical conditions differing largely with time and position in the loop, e.g. temperature gradients or increasing impurity concentration with time. Furthermore, we present results of small scale experiments on proton irradiated mercury, which show that indeed the distribution of nuclear reaction products is far from homogeneous, but substantial amounts of these products stick to the walls of the irradiation capsules. Those nuclides adherent to the liquid metal are not homogeneously distributed in Hg as well. Highly soluble noble metals like Ag and Au are actually dissolved in the liquid metal, while the remaining elements are located at the surface of the mercury droplet. Possible reasons for this behavior are discussed. Different methods for separation of nuclear reaction products from Hg have been tested on laboratory scale. The removal of solid material by high surface oxide material and the removal of dissolved components by metal absorbers looks promising. However, these procedures are still far from a technical mature state. Finally, we suggest a concept that could be feasible for an online removal of impurities from a liquid metal loop, based on our current state of knowledge. Advantages and disadvantages to more conventional purification procedures are discussed.

ACKNOWLEDGMENTS

This work was supported by the European Community under the FP6 "Research Infrastructure Action – Structuring the European Research Area" Project EURISOL DS under Contract No. 515768 RID IDS.

REFERENCES

1. <http://www.eurisol.org>
2. <http://isolde.web.cern.ch/ISOLDE/>
3. B. EICHLER and R. DRESSLER, "Löslichkeit von Kernreaktionsprodukten im Quecksilber-Spallations-target – Bedeutung für das Betriebsverhalten und Möglichkeiten der Kalkulation", PSI-Report No. 99-02, Paul Scherrer Institut, Villigen, Switzerland, 1999.
4. K. H. LIESER, *Nuclear and Radiochemistry: Fundamentals and Applications*, p. 269ff, VCH, Weinheim, Germany (1997).
5. F. R. DE BOER, R. BOOM, W. C. M. MATTENS, A. R. MIEDEMA, A. K. NIESSEN, *Cohesion in Metals, Transition Metal Alloys*, North-Holland, Amsterdam, The Netherlands (1988).