Removal of MoF$_6$ and HF from a helium-MoF$_6$ gas mixture

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Klydon developed an aerodynamic separation process (ASP) with the aim of establishing an industrial method for isotope enrichment with respect to molydenum-100 for medical usage. Helium is used as carrier gas for molybdenum, present in the form of molybdenum hexafluoride (MoF$_6$). MoF$_6$ is separated as product from the helium by freezing. The helium has to be purified subsequently and traces of hydrogen fluoride (HF) and MoF$_6$ have to be removed. Several gas separation technologies were considered with the final choice being the use of adsorbents, with emphasis on ion exchange resins. The reason for the choice was the fact that resins are easily obtainable synthetic polymeric materials, capable of exchanging or trapping specific ions. Because of the reactivity of both HF and MoF$_6$, it is more likely that both compounds will react irreversibly with the the solid resins. The experimental results indicated that MN102 and A100Mo showed potential for removal of MoF$_6$ from the helium stream in the final polishing step. The results were not suprising; A100Mo is a macroporous, mixed base-ion resin, used for removal of molybdenum form acid solutions, and MN102 is a macroporous, hydrophobic weak base-ion material. Alumina and activated carbon showed showed potential for removing HF. Further work is required for with mixtures of HF and MoF$_6$ to confirm the selective nature of the reactions.

Keywords: Adsorption, ion exchange resins, MoF$_6$, HF, MN102, A100Mo, alumina, activated carbon.

Verwydering van MoF$_6$ en HF uit 'n helium-MoF$_6$-gasmengsel: Klydon het die aërodinamiese skeidingsproses (ASP) met die doel van isotoopverryking in molibdeen-100 vir die doeleindes van mediese-isotoopproduksie ontwikkel. Helium word as draergas saam met molibdeen in die vorm van molibdeenheksafluoried (MoF$_6$) tydens die proses gebruik. Die MoF$_6$ word as produk uit die heliumstroom verwyder deur dit uit te vries. Die helium moet gesuiwer word en indien waterstoffluoried (HF) of MoF$_6$ nog teenwoordig is, moet dit effektief verwyder word. Nadat verskillende moontlikhede van gasskeiding en verwydering van HF en MoF$_6$ ondersoek is, het die keuse op adsorbente geval met die oorwig van keuse op ioonuitruilharse. Die rede vir die keuse was dat harse maklik bekombare sintetiese polimeermateriale is, wat in staat is om spesifieke ione uit te ruil of vas te lê. As gevolg van die reaktiwiteit van beide MoF$_6$ en HF, is dit meer waarskynlik dat die twee reagense onomkeerbaar met die vaste stowwe reageer. Die eksperimente het getoon dat MN102 en A100Mo potensiaal het om MoF$_6$ in die finale poleringsstap uit helium te verwyder. Verder het die eksperimente getoon dat alumina en koolstof moontlik die potensiaal het om HF selektief uit 'n heliumstroom te verwyder. Die resultate was nie verrassend nie want A100Mo is 'n makroporeuse, gemengde basisanioon hars, wat juis gebruik word om molibdeen uit suuroplossings te verwyder. MN102 is 'n makroporeuse hidrofobiese, swak basisanioon hars. Verdere studie en eksperimentering met 'n mengsel van HF en MoF$_6$ om die selektiewe reaksie van HF te ondersoek word dus sterk aanbeveel.

Sleutelwoorde: Adsorbsie, ioonuitruilharse, MoF$_6$, HF, MN102, A100Mo, alumina, koolstof.

Introduction

The global market for nuclear medicine, which includes radioisotopes and medical devices is expected to grow to nearly $20 billion by 2021. The decay product of Mo-99, Technetium-99m, is the most widely used medical radioisotope (Richards *et al.*, 1982). It is used annually as a radioactive trace element in more than 40 million medical diagnostic procedures. Tc-99m (the m indicates the meta-stable energy state) is unusual because it has a half-life of 6,03 hours, which is very long for electromagnetic decay. Usually it is 10^{-16} seconds (Aaseth *et al.*, 2016). The most common method of producing Mo-99 is by cleaving 235-U in a nuclear reactor. The Mo-99 decays with a half-life of 66 hours after the meta-stable state of Tc. This process allows the production of Tc-99 for medical purposes. The nuclear route to produce Mo-100 requires enriched uranium as fuel. A disadvantage of this method is the radioactive waste that forms, and challenges in the transport of radioactive molybdenum.

Concerns about the availability of Tc-99, especially after the unexpected, prolonged shutdown of the Chalk River (Canada) and Petten (Netherlands) reactors, and the disadvantages of the current nuclear reactor route of production have led to renewed interest in the cyclotron production of this isotope (IAEA, 2017). In the cyclotron process, Mo-100 is irradiated with protons to form Tc-99. The starting material for this route is 98% pure Mo-100 which must be separated from all its other isotopes and enriched to the necessary purity.

The aerodynamic separation process (ASP technology) of Klydon is suitable for separating components of a gas mixture or different isotopes of a specific gas compound based on the mass difference of the gas components or the isotopes. Klydon uses high-speed centrifugal rotation of the gas or isotope mixture in a stationary wall centrifuge with no moving mechanical parts. Helium is used as a carrier gas together with molybdenum in the form of molybdenum hexafluoride (MoF_6) during ASP separation. The advantage of ASP technology is that a stable, non-radioactive Mo-100 isotope is formed. The Mo-100 is converted in a cyclotron to Tc-99 (Ronander *et al.*, 2012).

After the separation process and freezing of the desired product, it is estimated that approximately 0,0009 mole fraction (a mass fraction of 0,045) of MoF_6 remains in the helium gas stream.

Although all possible precautions have been taken to limit the formation of HF, there is a high probability that the helium gas stream may contain small amounts of HF. If HF has formed, it must be effectively removed from the system. All MoF_6 and HF must be removed in the final polishing step as the helium is reused with ASP technology. If there is still MoF_6 present in the helium that is reused, it leads to loss in separation work from the plant. The HF and MoF_6 that are removed in the final polishing step are not reused.

However, it may make sense to investigate the reuse of MoF_6 from the adsorbent in further studies.

The sorption of a variety of resins and adsorbents was investigated for this study, with the aim to determine the capacity for the uptake of HF and MoF_6 from the solid materials. Twelve different typical adsorbents were selected and experiments were performed and data of pressure and temperature versus time were collected. The main advantage of the method is that impurities are removed from the helium stream in a relatively simple manner.

Material
Molybdenum hexafluoride MoF$_6$

At room temperature, MoF_6 is a colourless, volatile liquid with a molar mass of 209,93 g/mol. MoF_6 is used in its gaseous form to separate isotopes from molybdenum using the aerodynamic separation process to produce Mo-99. The MoF_6 hydrolyses rapidly to form hydrogen fluoride (HF) and molybdenum oxides. The formation of HF is accompanied by the reduction of MoF_6 to lower oxidation conditions and should be avoided. Locally, F_2 and MoF_6 are manufactured by Necsa.

HF
Dangers of HF

The formation and release of HF, hydrogen fluoride, are extremely dangerous and should be avoided at all costs. The danger of HF is due to the physicochemical properties of HF and the specific attack of HF on living tissue.

HF has a strong H — F bond, causing the compound to be very stable, as evident from its pKa value of 3,19 (O'Neil, 2013). The H — F ---- H — F hydrogen bond exists in the gas phase and leads to large deviation from ideality and is responsible for the high boiling point of the substance. The gas phase HF is one of the species that deviates the most strongly from ideality.

Hydrofluoric acid is extremely corrosive which should be taken into consideration in experimental setups. Like other acids, aqueous HF is corrosive to several common, industrial materials including iron, stainless steel, copper, glass, asbestos, concrete and natural rubber. Most metals react with AHF (anhydrous hydrogen fluoride) to form metal fluorides and hydrogen.

Stainless steel adsorbs moisture on its surface and forms oxyhydroxides. This moisture may be gassed during use and therefore stainless steel must be treated to passivate the surface of the steel by removing adsorbed and absorbed moisture and improving the corrosion resistance to corrosive materials. According to Davidson *et al.* (1991), the best results in surface passivation treatment are obtained if the surface to be treated is rinsed with a dry chemically non-reactive gas containing no oxygen, while the steel is baked for a predetermined time and temperature and then

cooled. According to Fine *et al*. (1994), atmospheric moisture easily condenses on metal surfaces in several layers. Under normal atmospheric conditions, which is 20 °C (293,15 K) and absolute pressure of 1 atm (101,325 kPa), less than one molecular layer of oxygen or nitrogen will be physically adsorbed on a metal surface. Under the same conditions, multiple molecular layers of moisture will adsorb on the metal. This strong adsorption of multiple layers of moisture makes the removal of moisture from a system a very difficult task. Systems are heated to a high temperature to remove moisture. However, heating is not always practical, and it does nothing to prevent re-adsorption of water if the system is re-exposed to the environment.

If metal surfaces are not dried sufficiently, the molybdenum hexafluoride will react with the surface water to form molybdenum trioxide and hydrogen fluoride:

$$3H_2O + MoF_6 \rightarrow MoO_3 + 6HF$$
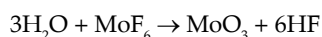
Passivation

The passivation procedure briefly involves the careful exposure of the plant to a dilute fluorine gas mixture at different pressures for certain periods of time. The passivated system is maintained at a helium overpressure and must be protected against exposure to moisture and contamination.

Sorbents

After careful consideration, the following solids were selected to determine their ability to remove HF and MoF_6 from the He stream:

Seven resins, *viz.* A110, A111, A870, S984 A850FL, MN102 A100Mo, two adsorbents *viz*. CCP510 and CCP310, alumina, activated carbon and bentonite.

Ion exchange resins consist of two main types, *viz.* cation exchange resins that exchange positively charged ions, such as sodium, and anion exchange resins, which exchange negatively charged ions, such as chloride. The backbone of resins is usually a polystyrene polymer and they differ only according to their specific functional groups (Vagliasindi *et al*., 1998). The resins were kindly supplied by Purolite. The adsorbents CCP 310 and CCP 510 were supplied by Freudenberg Filtration Technologies. The bentonite was sourced from Yellow Star Bentonite near Parys, Free State. The properties of the resins, adsorbents and bentonite are summarised in Table 1.

Experimental method

A test loop was designed and commissioned. See Figure 1. The loop is positioned in an electric oven so that drying can take place by heat treatment.

About 0,05 g of resin was used at a time. The resins were dried in a drying oven overnight, at the correct temperature according to each resin.

A manometric method was used to determine adsorption capacity. The principle of volumetric gas adsorption is simple: a given amount of gas is released into the reactor which is initially evacuated and which includes a sample of the adsorbent. The gas is adsorbed on the (external and internal) surface of the adsorbent material. Mass balance and the ideal gas equation are used to calculate the amount of gas that is adsorbed (Keller & Staudt, 2005).

Two reactors, Reactor 1 and Reactor 2, made of stainless steel, with flanges so that they could be closed airtightly, were equipped with pressure gauges and temperature couplings. Valve 1 was installed between the gas supply and the MoF_6 storage tank (Reactor 1) and Valve 2 between the two reactors. Valve 3 was installed between the test bench and the manifold. The manifold supplies helium and MoF_6 gas and the effluent to a calcium carbonate chemical trap. Reactor 1 was charged with the gas while Valve 2 was closed to Reactor 2 which contained the adsorbent. Since the volume of Reactor 1 was known, the number of moles of gas could be calculated using the ideal gas equation. After charging the gas and determining pressure and temperature, Valve 2 was opened between Reactor 1 and Reactor 2. In Reactor 2, the adsorbent, which had been pre-dried and weighed, was placed. The volume of Reactor 2 was also known. The change in pressure and temperature were used to determine how much gas had been adsorbed by adsorbent. In this way, the adsorption capacity of a specific adsorbent could be determined.

The ideal gas law was used to calculate the number of moles initially present by using the pressure at the moment Valve 2 was opened.

It was difficult to exactly control the initial pressure. It was typically between 10 and 20 kPa. All experiments were performed without temperature control. Experiments were started at room temperature, and thereafter the temperature
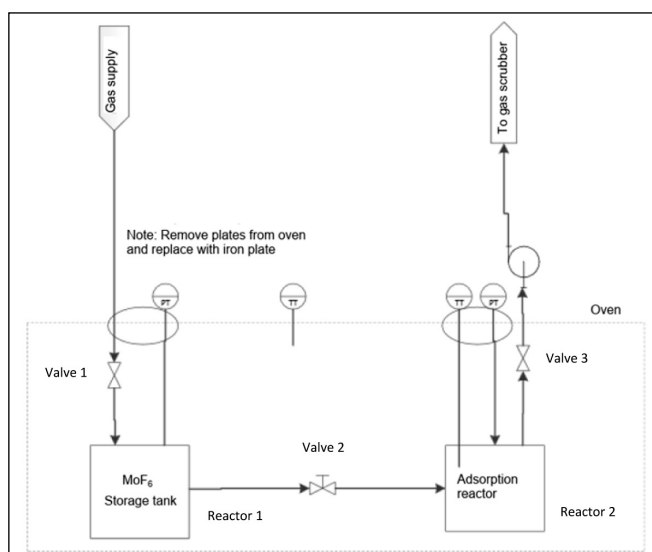

FIGURE 1: Pipe and instrumentation diagram (P&ID) of the adsorbent test loop

was monitored continuously. The pressure was monitored until steady state was reached, typically after 8 to 20 minutes. The pressure was in excess in all cases to determine the amount of gas reacted/adsorbed from the difference between the initial and final pressures. As mentioned above, substantially constant masses, 0,05 g, adsorbent/solid reagent were used for all experiments.

Results and discussion

Results are tabulated in Table 2 below.

A110 was chosen because it is a macroporous polystyrene cross-linked with divinylbenzene which can remove acid and colour. The ionic form is a free base with primary amine as the functional group. The temperature limit of 60 °C facilitates drying of the adsorbent granules. The adsorption capacity of A110 was calculated as 0,842 g MoF_6 per gram adsorbent.

A111 was chosen because it is a macroporous polystyrene crosslinked with divinylbenzene used for demineralisation. The ionic form is a free base with tertiary amine as the functional group. Drying is facilitated with the temperature limit of 60 °C. Although the adsorbent turned black due to adsorption of excess MoF_6, the grains still retained their shape and did not sinter. The adsorption capacity of A111 was calculated as 1,30 g MoF_6 per gram adsorbent.

Like A111, A100Mo is a macroporous polystyrene cross-linked with divinylbenzene used for demineralisation. The ionic form is also a free base with tertiary amine as the functional group. Drying is facilitated with the temperature limit of 60 °C. To determine the adsorption capacity of A100Mo, only 0,0339 g of adsorbent and 0,0006 mol of MoF_6 were used so that MoF_6 was in excess. The adsorption capacity of A100Mo was then 2,17 g gas/gram adsorbent.

MN102 is also a macroporous polystyrene cross-linked with divinylbenzene with the ionic form a free base with tertiary amine as functional group. The grains are dark brown and are used for demineralisation. Drying is facilitated with the temperature limit of 60 °C. To calculate the adsorption capacity of MN102, MoF_6 must be present in excess. After using only 0,01 g of adsorbent and 0,00071 mol of MoF_6, the adsorption capacity of MN102 was calculated as 3,30 g of gas/gram of adsorbent.

S984 was chosen because a macroporous polyacrylic crosslinked with divinylbenzene is used for the removal of heavy metals and anions. The ionic form is a free base with polyamines as the functional group. Some of the white granules discoloured to dark blue after adsorption. After using only 0,0577 g of adsorbent, so that the adsorbent was present in excess, and all the MoF_6 was not adsorbed, the adsorption capacity of S984 was calculated as 2,34 g of MoF_6 per gram of adsorbent. As observed, the granules retained their physical properties after adsorption and only colour change and mass increase occurred.

A870 is a gel polyacrylic, cross-linked with divinylbenzene. Quaternary and tertiary amines act as functional groups. The temperature limit of the gel polyacrylic is 35 °C and as such, it cannot be dried in the oven and appeared damp. It is used to remove organic matter, strong acids and weak acids. The yellowish grains remained moist and discoloured. The reaction was exothermic and occurred very rapidly giving rise to the suspicion that the moisture

TABLE 1: Summary information of adsorbents

Name	Polymer structure	Functional group	Ionic form	Particle size	SG	Temperature limit	Application
A110	Macroporous polystyrene cross-linked with divinylbenzene	Primary amines	Free base (FB)	300 – 1 200 µm	1,07	60 °C	Acid and colour removal. CO_2 and aldehyde adsorption.
A111	Macroporous polystyrene cross-linked with divinylbenzene	Tertiary amines	Free base (FB)	300 – 1 200 µm	1,02	100 °C Cl- form 60 °C FB form	Demineralisation.
A870	Gel polyacrylic, cross-linked with divinylbenzene	Quaternary and tertiary amines	FB or Cl- form	300 – 1 200 µm	1,08	35 °C	Organic matter, strong and weak acid removal.
S984	Macroporous polystyrene cross-linked with divinylbenzene	Polyamines	Free base (FB)	300 – 1 200 µm	1,1		Removal of heavy metals and anions.
A850FL	Gel polyacrylic, cross-linked with divinylbenzene	Quaternary amines	Cl- form	500 – 1 000 µm	1,09	35 °C	Demineralisation.
MN102	Macroporous polystyrene cross-linked with divinylbenzene	Tertiary amines	Free base (FB)	535 ± 85 µm	1,07	60 °C FB form	Sorption, hydrophobic, organic species separation.
A100Mo	Macroporous polystyrene cross-linked with divinylbenzene	Tertiary amines	Free base (FB)	0,6 – 0,85 nm	1,04	60 ° FB formC	Demineralisation.
Activated alumina	Highly porous ceramic-like compound.			5 mm – 8 mm	0,75		Removal of water vapour from air, industrial gases, CO_2, natural and cracked gas streams.
Carbon Carbosorb	Large surface area. A large number of micropores.			1,5 mm- 4 mm			Gas purification and separation.
Bentonite	Lamellar three-layer mineral with two tetrahedral layers surrounding a central octahedral layer			Layers 1 nm in thickness and 2 micron in diameter			

TABLE 2: Tabulated results

Adsorbent	Polymer structure	Functional group	Properties	Adsorption capacity (mass MoF$_6$/gram adsorbent)	Recommendation
A110	Macroporous polystyrene crosslinked with divinylbenzene	Primary amine	Temperature limit 60 °C. Properties remain intact after adsorption. No sintering.	0,85 g	Features make it a good choice.
A111	Macroporous polystyrene crosslinked with divinylbenzene	Tertiary amines	Temperature limit 60 °C. Properties remain intact after adsorption. No sintering.	1,875 g	Properties and good adsorption capacity make it an excellent choice.
A100Mo	Macroporous polystyrene crosslinked with divinylbenzene	Tertiary amines	Temperature limit 60 ° C. Properties remain intact after adsorption. No sintering.	2,276 g	Properties and excellent adsorption capacity make it an excellent choice.
MN102	Macroporous polystyrene crosslinked with divinylbenzene	Tertiary amines	Temperature limit 60 ° C. Properties remain intact after adsorption. No sintering.	3,293 g	Properties and excellent adsorption capacity make it an excellent choice.
S984	Macroporous polyacrylic crosslinked with divinylbenzene	Polyamines	Poor adsorbing ability	0,41 g	Poor adsorbing ability does not make it a good choice.
A870	Gel polyacrylic crosslinked with divinylbenzene	Quaternary and tertiary amines	The gel does not react well with gas.	0,465 g	Gel and moisture make it a poor choice.
A850FL	Gel polyacrylic crosslinked with divinylbenzene.	Quaternary amines	The gel does not react well with gas.	0,736 g	Gel and moisture make it a poor choice.
Bentonite	Clay mineral consisting of montmorillonite.		High temperature limit but clay properties after adsorption under suspicion.	0,619 g	Uncertainty about clay properties makes it a risky choice.
Alumina	Very porous ceramic-like compound.		High temperature limit but poor adsorption capacity	0,241 g	Important adsorbent to further investigate for selective adsorption of HF.
Carbon	Activated carbon with micropore structure.		High temperature limit but poor adsorption capacity	0,457 g	Important adsorbent to further investigate for selective adsorption of HF.
CCP 510 (Alphasorb 5)	Porous structure made of activated alumina with active ingredients.		Poor adsorbing ability	- 0,127 g	Poor adsorption capacity makes adsorbent a poor choice.
CCP 310 (Alphasorb 15)	The porous structure of CCP 310 granules is activated alumina impregnated with activated carbon.		Poor adsorbing ability	0,144 g	Poor adsorption capacity makes adsorbent a poor choice.

reacted with MoF$_6$ to form HF. The adsorption capacity under the conditions was only 0,0114 g MoF$_6$/gram adsorbent.

A850FL is also a gel polyacrylic, cross-linked with divinyl-benzene. Quaternary ammonium acts as a functional group. The temperature limit of the gel polyacrylic is 35 °C and as such it cannot be dried in the oven and the granules remain moist. It is used for demineralisation. The granules appeared moist after adsorption with solid pieces on the outside. However, the temperature remained fairly constant. The adsorption capacity of A850FL was 0,7356 g MoF$_6$ per gram adsorbent.

Bentonite which has several adsorption applications due to its channel structure, is readily available, inexpensive and has a good capacity, and therefore it was decided to use it. The bentonite was readily available but unfortunately only in powder form. The formation of granules small enough with the same shape and size was problematic. An interesting colour change occurred during adsorption. The adsorption capacity of the bentonite was 0,340 g MoF$_6$ per gram adsorbent.

Activated alumina consists of white granules and is a highly porous product that can absorb both gases and liquids without changing shape or disintegrating. Another common use is for the removal of fluorides from water. ZT-200 is used for removing water vapour from air, industrial gases, CO$_2$, natural and cracked gas streams. The adsorption capacity of alumina was 0,24 g MoF$_6$ per gram adsorbent. The granules had blue parts after adsorption but turned yellow-green after exposure to air. The reduction of MoF$_6$ leads to the production of MoF$_4$, a light green substance that could possibly explain the discolouration.

According to Chattopadhyay and Das (2008), the capacity of alumina to adsorb Mo is limited (20 mg Mo/g alumina) and large alumina columns are needed to convert molybdenum into both the Mo-99/Tc-99m as well as the W/Re -188 generators to adsorb, but due to its positive properties, it was decided to do a further test with alumina and to investigate the adsorption capacity of alumina against HF gas. The experiment was repeated with 0,6062 g HF released from KF·HF. Only 0,27269 g of alumina was used. Thus, 2,208 g of HF was adsorbed per gram of adsorbent. Comparatively, the adsorption capacity of

alumina versus MoF_6 was 0,2405 g gas/gram adsorbent. It therefore appears to be an important adsorbent to be further investigated for selective adsorption of HF.

The exceptional hardness, low flow resistance, low density and high working capacity made carbon a cost-effective choice. Activated carbon is extremely porous with a very large specific surface area. Activated carbon can have a surface area of more than 1000 m^2/g. This means that 5 g of activated carbon can have the surface of a rugby field (Cheremisinoff, 2001). The adsorption capacity of carbon was 0,457 g MoF_6 per gram adsorbent. The reason why activated carbon is such an effective adsorption material is due to the large number of pores. It offers a large surface area in relation to the size of the actual carbon particle and its visible outer surface. For these reasons it was decided to also use activated carbon to investigate the adsorption capacity of the carbon against HF. KF·HF was used to generate HF. In Reactor 1 4,5227 g KF·HF was placed and, at the same time, 0,4587 g carbon was placed as an adsorbent in Reactor 2. The valve between Reactor 1 and Reactor 2 was closed and the furnace was switched on at 50 °C. After half an hour the temperature was raised to 100 °C, half an hour later to 150 °C and half an hour later to 175 °C. Half an hour after oven temperature was set at 175 °C, Valve 2 between Reactor 1 and 2 was opened and the oven was switched off. The pressure increase from 4,98 kPa to 22,61 kPa, i.e. 17,63 kPa, was observed. The volume of the container was 0,0515 dm^3. The carbon was weighed after completion of the experiment and it was determined that 0,0049 g of gas had been adsorbed. Thus, the adsorption capacity of carbon to HF is 1,22 g HF/gram carbon. Comparatively, the adsorption capacity of carbon versus MoF_6 is 0,457 g MoF_6 per gram adsorbent. Carbon can therefore be further investigated as a possible adsorbent to selectively remove HF from MoF_6 helium gas mixture.

CCP 510 granules are white and are specifically used for removal of gas halogens from air by adsorption and absorption within the porous structure made of activated alumina with active ingredients. The number of moles of gas initially increased which may mean that CCP510 secreted gas. What could be clearly observed was that it did not adsorb MoF_6 successfully at all. Therefore, no further tests were performed with CCP510.

CCP 310 granules are used for the filtration of acid gases in corrosive environments. It is activated alumina impregnated with activated carbon evenly distributed throughout the grain for high efficiency for long life, according to the manufacturer. From processed data, it was calculated that only 0,144 g gas/gram adsorbent was adsorbed. Furthermore, it was observed to be an exothermic reaction and for these two reasons, it was decided not to experiment further with CCP 310.

The use of MoF_6 caused several problems. The operation of the valves was difficult, the reactors had to be cleaned regularly in ultrasonic baths due to the formation of oxyfluorides and the pressure gauge in Reactor 2 failed.

MoF_6 is an extremely strong fluorinating agent and this made the choice of contraction materials problematic. A further challenge it caused was the failure of equipment due to oxyfluoride precipitation that formed in the pressure gauges and valves. The reactors also had to be cleaned after every few experimental runs in an ultrasonic bath to remove the precipitate that formed. The precipitation also affected the mass increase of the adsorbents. There was thus a mass loss due to precipitation formation present. An additional challenge was that the equipment was not designed to be able to observe the mass increase and colour change before exposure to the atmosphere. This affected the determination of the mass increase of the adsorbents because, due to hydrolysis and oxidation of the adsorbents the moment the reactor was opened, the determination of the mass increase was not 100% correct. However, the error was a constant error for all the adsorbents and as such did not affect the choice of the most suitable adsorbent. The colour of the adsorbents also changed with exposure to the atmosphere.

The resins, adsorbents, carbon, alumina and bentonite retained their morphology excellently during the experiments. The pressure drop observed during the experiments showed that there was an interaction between the MoF_6 gas and the adsorbent. This was either due to adsorption or a chemical reaction between MoF_6 and the solid. The only material where the pressure really flattened to constant pressure was with carbon. The pressure of the other adsorbents did not reach steady state conditions. A possible conclusion is that carbon was the only adsorbent, and chemical reactions had taken place with the other materials, and not adsorption. The most likely mechanism was mass transfer control through the product layer. Further investigations specifically for carbon to curve fit with the Langmuir adsorption equation are recommended to determine the equilibrium constant as a function of temperature. The colour change and possible products that caused the colour change in the other materials are summarised in Table 3 below.

Summary

The sorption capacity of a variety of resins and adsorbents was investigated for this study, with the aim of determining the capacity for the uptake of HF and MoF_6 from these materials. Twelve different typical commercial adsorbents were selected and their capacities were determined from print-time data collected. Temperature was monitored, not controlled. The main findings are as follows:

The adsorption capacity of A100Mo was 2,276 g MoF_6 per gram adsorbent and that of MN102 was 3,293 g MoF_6 per

TABLE 3: Colour change of adsorbents and possible explanation

Adsorbent	Colour change	Possible product formed
A110	Green blue but dark blue if excess MoF6 is present.	MoF_4 is light green which may explain green blue.
		$Mo_2O_5 \cdot xH_2O$ is dark blue which may explain dark blue colour when MoF_6 is in excess.
A111	Green blue but black if excess MoF6 is present.	MoF_4 is light green which may explain green blue.
		Mo_2O_3 is black which may explain black colour.
A100Mo	Green blue.	MoF_4 is light green which may explain green blue.
MN102	Dark blue to black.	$Mo_2O_5 \cdot xH_2O$ is dark blue which may explain dark blue colour.
		Mo_2O_3 is black which may explain black colour.
S984	Green blue and dark blue.	MoF_4 light green which may explain green blue.
		$Mo_2O_5 \cdot xH_2O$ is dark blue which may explain dark blue colour when MoF_6 is in excess.
A870	Dark blue and black.	$Mo_2O_5 \cdot xH_2O$ is dark blue which may explain the blue colour.
		Mo_2O_3 is black which may explain black colour.
A850FL	Cobalt blue precipitation on the grains.	$Mo_2O_5 \cdot xH_2O$ is dark blue which may explain precipitaion.
Bentonite	Yellow colour.	MoO_5 as well as $MoO_2 \cdot 2H_2O$ are yellow.
Alumina	Blue to yellow-green.	MoO_5 as well as $MoO_2 \cdot 2H_2O$ are yellow.
		MoF_4 is light green which may explain green blue.
Activated carbon	No observation possible with black carbon.	
CCP510	Dark blue, yellow-green and black spots are observable on grains.	$Mo_2O_5 \cdot xH_2O$ is dark blue which may explain the blue colour.
		Mo_2O_3 is black which may explain black colour.
CCP310	Black.	Mo_2O_3 is black which may explain black colour.

gram adsorbent. Following experimental results, it is recommended that MN102 and A100Mo be further investigated for use as adsorbent in the final polishing step to remove MoF_6 from helium.

The adsorption capacity of alumina versus HF was calculated as 2,208 g HF per gram of alumina. When compared to adsorbent capacity of alumina versus MoF_6 which is 0,2405 g gas per gram adsorbent, it is an important adsorbent to investigate to obtain selective adsorption of HF from helium.

The adsorption capacity of carbon versus HF is 1,22 g HF per gram of carbon. Comparatively, the adsorption capacity of carbon versus MoF_6 was 0,457 g MoF_6 per gram of adsorbent which also makes it possible to investigate selectively removing HF from MoF_6 helium gas mixture. Further tests with alumina and carbon as a selective adsorbent to remove HF from helium stream are recommended.

The results presented here are, of course, exploratory in nature, and a complete understanding of the chemistry involved was not possible with the resources and time at our disposal. HF and MoF_6 are both extremely reactive. Although we use adsorption and reaction as synonyms, it is clear that in most cases strong reactions take place. The characterisation of the solid products that form is extremely problematic. In general, the products are hygroscopic and undergo rapid reaction as soon as atmospheric exposure occurs. The complete characterisation would therefore require, before each analysis, special sample containers manufactured specifically for each analytical instrument.

The main advantage of the method is that we have shown that impurities can be removed from the helium stream in a relatively simple manner, and that the helium can then be recycled.

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