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## REVIEW

# Composite sorbents of inorganic ion-exchangers and polyacrylonitrile binding matrix

## I. Methods of modification of properties of inorganic ion-exchangers for application in column packed beds

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Methods of preparation of granules of inorganic ion exchangers as well as methods for improvement of granular strength of these materials are reviewed. The resulting ion exchangers are classified in three groups – "intrinsic", supported and composite ion exchangers. Their properties are compared and possibilities of their technological application are evaluated. A new method of preparation of inorganic–organic composite sorbents of inorganic ion-exchangers and polyacrylonitrile binding matrix is described, advantages and disadvantages of such sorbents are discussed. Proposed fields of application include tratment of liquid radioactive and/or hazardous wastes, decontamination of natural water as well as analytical applications.

### Introduction

The use of inorganic ion-exchangers for treating liquid radioactive wastes has recently become again more prospective. These exchangers are promising advanced new technologies that should ensure greater safety and lower cost.[1] Areas of possible application of inorganic ion-exchangers were recently evaluated by HOOPER et al.,[2] who also specified the exact requirements that prospective sorbents should fulfil.

Inorganic ion-exchangers exhibit a broad variety of advantageous properties when compared with synthetic organic ion-exchangers. Their main advantage is their high selectivity for the capture of certain ions. Greater thermal and radiation stabilities, often good chemical stability even in strongly acidic media, and compatibility with matrices used for their immobilisation can be listed among other advantages. The most serious disadvantages of synthetic inorganic ion exchangers are their unsuitable granulometric and mechanical properties that limit their use in column applications.

Many different methods have been proposed for preparing granules of inorganic ion-exchangers and for improving granular strength of these materials. On the basis of the preparation method used, the resulting ion exchangers can be classified in three groups:

"Intrinsic" inorganic ion exchangers represent a group of ion-exchangers prepared without use of any additives.

Supported ion exchangers represent a group of inorganic ion-exchangers, in which the active inorganic component is deposited on a suitable "supporting" material.

Composite ion exchangers represent the group of inorganic ion-exchangers modified by a binding material to prepare larger particles with higher granular strength.

Complex evaluation of the suitability of these three groups of synthetic inorganic ion-exchangers for treating liquid radioactive wastes is rather difficult. Each of these groups exhibits certain advantageous properties, the use of each of them has some more or less serious draw backs.

In the following parts of this contribution examples of ways of preparation of granular sorbents from single (as defined above) groups are provided. Their properties are compared, and possibilities for their technological application are evaluated. The given survey is not complete, its primary aim is to summarise and provide examples of the published methods for modifying inorganic ion-exchangers for use in column packed beds. In the last part of this paper, a new method for preparing inorganic-organic composite absorbers consisting of inorganic ion-exchangers and polyacrylonitrile binding matrix is described, advantages and disadvantages of such absorbers are discussed.

### "Intrinsic" sorbents

#### *Natural inorganic ion-exchangers*

Natural inorganic ion-exchangers are usually modified for use in column packed beds by crushing, followed by sieving to obtain particles of the required size. In the last step, the fine particles are washed out by flushing the absorber by water. Examples of natural zeolites often used for treating liquid radioactive wastes are clinoptilolite, mordenite, and chabazite. Their main advantage is their low price, the main disadvantages are their not exactly defined structures, low capacities, and impure chemical compositions.

#### *Synthetic inorganic ion-exchangers*

Synthetic inorganic ion-exchangers are insoluble inorganic compounds prepared by precipitation, usually in aqueous solutions. Depending on the specific absorber prepared (type of chemical compound and method of preparation), their structure may be crystalline or amorphous. Most advantageous are those that can be

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prepared as sufficiently large crystalline particles to be directly used as column bed material.

Unfortunately, only a few inorganic ion-exchangers can be prepared in such suitable crystalline form.[3,4] In most cases, the precipitated inorganic ion-exchanger must be separated by filtration and the undesirable chemical admixtures washed out. Suitable granules are obtained by sieving the dried, crushed filtration cake to obtain a fraction with requested grain size. The finest particles are washed out of the granules (e.g., by decantation) before application. Veselý and Pekárek state[3,4] that many granular inorganic ion-exchangers can be prepared using this procedure.

An overview of preparation of granular metal hexacyanoferrates by this procedure was published by Jacobi.[5] Many inorganic ion-exchangers commercially supplied by STMI-RAN (France)[6] are obviously prepared in this way. The most commonly used absorber prepared by this procedure is cobalt-potassium hexacyanoferrate KCFC, proposed by Prout et al.[7] Currently, KCFC is used in the large-scale treatment of liquid radioactive wastes at the Loviisa Nuclear Power Plant (NPP) in Finland.[8]

A technical disadvantage of the described procedure is the substantial loss of material as dust and particles smaller than the required grain size. Moreover, granules produced by this method undergo sometime decomposition during the contact with the treated solution (e.g., by peptisation). This phenomenon may cause increased resistance of the column bed, resulting in decreased flow rate or even column clogging. Drying the filtration cake at an elevated temperature (a usual step of this procedure) has a significant negative influence on the kinetics of ion-exchange and sorption capacity of the resulting absorber.

In some cases (microcrystalline precipitates), it is not possible at all to produce an absorber with sufficient mechanical strength using the above described procedure. For this reason, the special methods discussed of modification of inorganic ion-exchangers below were developed.

*Slow-growth method:* Under normal circumstances, ammonium salts of heteropolyacids may be prepared only in the form of very small crystals (~200 mesh). A procedure for preparing larger particles (0.4 mm), described by Smith,[9] consists of contacting crystals of molybdophosphoric acid with a concentrated solution of ammonium nitrate. Relatively strong agglomerates of ammonium salt result. Their mechanical strength is sufficient to withstand several sorption-desorption cycles. A similar method was used by Berák[10] for preparing granules of barium sulphate activated by calcium. He contacted crushed calcium sulphate (as the natural mineral anhydrite or gypsum), loaded in a chromatographic column, with a solution of a barium salt.

The slow-growth method has also been used to prepare zinc or nickel hexacyanoferrates(II).[11,12] In this method, local growth occurs on sodium or potassium ferrocyanide crystals placed in concentrated zinc or nickel solution to produce hollow spheres. Particles of 0.1 to 0.5 mm can easily be prepared. The mechanical resistance of zinc-potassium ferrocyanide loaded column was sufficient for processing a solution of 20 000 bed volumes. The chemical stability was verified for zinc ferrocyanide in solutions from pH 1 to 10 and for nickel ferrocyanide from pH 0 to 12. The limiting factor in using hexacyanoferrate(II) salts prepared in this way is a partial release of zinc or nickel cations from the absorber.

*High temperature treatment:* An intrinsic absorber containing barium sulphate, activated by calcium, was prepared by heating a mixture of barium and calcium sulphates at 1000 to 1300 °C. After cooling the molten mixture, the solid product was crushed and processed in the usual way to a obtain granular material.[13,14] A similar method was used to prepare potassium titanate fibres from a molten mixture of potassium carbonate and titanium oxide.[15] Hydrothermal treatment for 20 hours at 200 to 300 °C was used to increase the crystallinity of sodium titanate.[16]

*Freeze-thaw method:* This procedure was used to produce granules from inorganic ion-exchangers yielding amorphous precipitates that settle and filter poorly. The method makes use of the fact that water is irreversibly separated when a gel (precipitate) is frozen, and the absorber becomes granular. After thawing, the granules are separated from the solution and air-dried at ambient or elevated temperature. This method has been used to prepare various granular hydrated oxides – $SnO_2$, $SiO_2$, $MnO_2$, $TiO_2$, $ZrO_2$, $Fe_2O_3$, and mixed absorbers[17] – nickel hexacyanoferrate + $Ni(OH)_2$, PbS + + $Pb(OH)_2$, NiS + $Ni(OH)_2$.

It has been also used to prepare granular zirconyl phosphate[18,19] and various hexacyanoferrates.[20,5] Jacobi[5] performed a very detailed study of the possibilities for preparing nickel-sodium hexacyanoferrate. He concluded that the conditions under which the prepared precipitates are frozen are crucial to obtaining a product in good granular form. The product prepared has good sorption properties for caesium but is completely stable only in the range of pH 4 to 10. Below pH ~4, nickel is released from the material, above pH ~10, the material decomposes.

*Sol-gel method:* The use of the sol-gel technique to prepare spherical particles of inorganic ion-exchangers was a significant contribution to developing procedures for modifying their granulometric and mechanical properties. This method makes use of converting a sol (or even a true solution), dispersed in an organic solvent, to hydroxidic gel.[21–23] From the principle of the method it follows, that it is possible to prepare uniform spheres of hydroxidic gels from only polyvalent hydrolysable cations, e.g. $Al^{3+}$, $Fe^{3+}$, $Cr^{3+}$, $Si^{4+}$, $Ti^{4+}$, $Zr^{4+}$, or their mixtures.

The conversion of a sol into a gel may be accomplished by either internal or external gelation.[21,23] Internal gelation is generally used to prepare intrinsic absorbers. Sols may be dispersed in media that are immiscible with water (paraffin or silicon oils, kerosene, etc.) in chemical reactors equipped with good stirring capability, or in continuous gelation columns by dripping from capillaries.[23]

To extend the scale of inorganic ion-exchangers that can be prepared with the sol-gel method, a procedure for

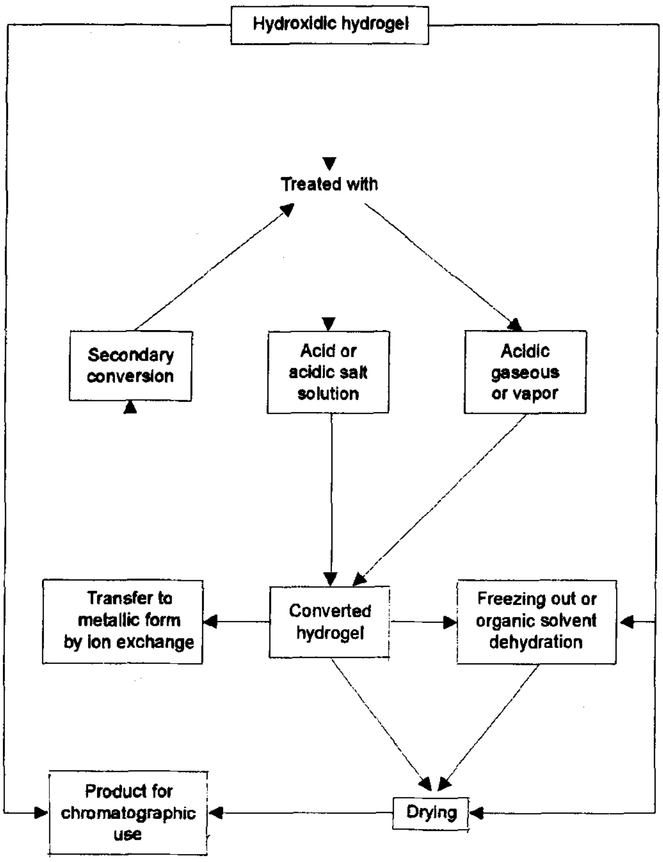

*Fig. 1.* Flow-chart for converting gel spheres[22]

converting primarily prepared hydroxidic gels was proposed and developed.[21,22] The chemical flow-chart for converting gel spheres is shown in Fig. 1. This method substantially increased the number of types and combinations of inorganic ion-exchangers that can be prepared with the sol-gel method.[22] For illustration, Fig. 2 presents a flow-chart for preparing titanium phosphate gel.

Among the disadvantages of the sol-gel method is the great shrinkage of particles after drying of hydrogels, or their conversion to xerogels. Moreover, the procedure is not universal; for example, it is not possible to prepare zinc or nickel hexacyanoferrates by this method.[12]

In addition, it should be reminded that spherical particles of inorganic ion-exchangers prepared by the sol-gel technique may contain also some insoluble organic impurities. For example, in the internal gelation procedure condensation products of urea and formaldehyde are produced.[24]

## Supported sorbents

Many materials have been proposed as suitable supports for inorganic ion-exchangers. Inert behaviour is a general and mandatory criterion for these materials; that is, no ion exchange or sorption should take place on the support materials. The simplest way to prepare supported sorbents is to either mix the fine-grained, or amorphous, precipitate of the ion-exchanger with an inert support material or induce it to precipitate directly on a suitable support. Among materials initially used as supports, asbestos, charcoal, alumina, filtration paper, glass fibres, glass wadding, and other porous materials can be listed.[3,4]

The main disadvantage of these procedures is a considerable increase in volume and problems with the loading larger columns. The sorption capacity of the resulting columns is usually too low, and the ion-exchangers may be washed out of the bed when they are used for longer periods.

Later, *silica gel* was proposed and used as a more suitable support for inorganic ion-exchangers. In this case, inorganic ion-exchangers were deposited on silica gel of a suitable grain size. CALETKA et al.[25–28] used silica gel as the support for various inorganic ion-exchangers. They proposed procedures for depositing several hexacyanoferrates on different types of silica gel.[25] Their intent was to develop the optimum procedure for producing

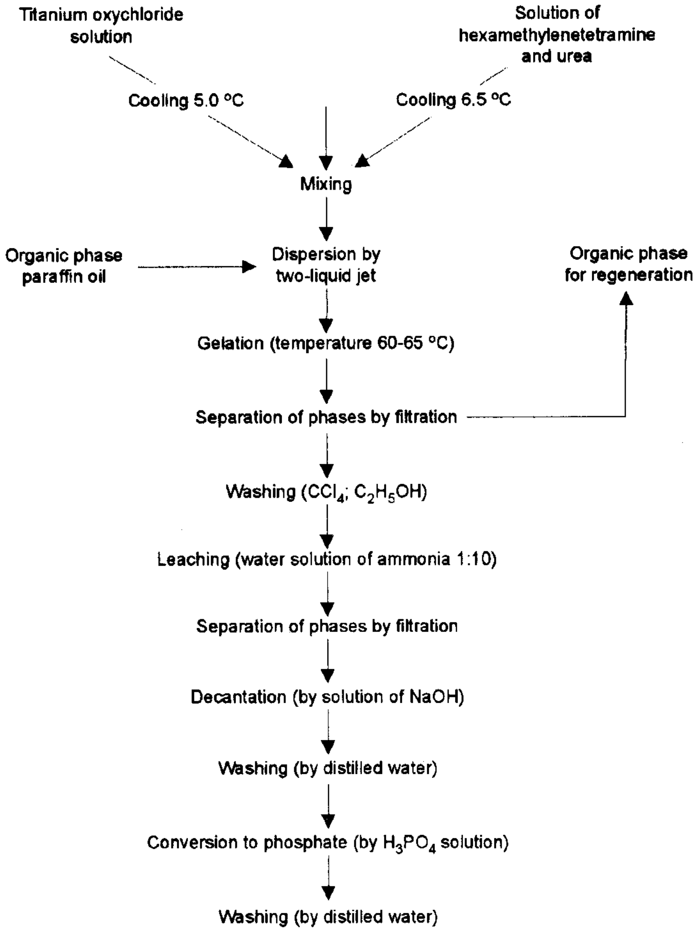

*Fig. 2.* Flow-chart for preparing titanium phosphate gel[23]

sorbents with the highest sorption capacity. In addition, they studied the ion-exchange properties of phosphoantimonic acid prepared by various procedures and deposited on silica gel.[26] This absorber was proposed for separating alkaline metals and strontium from acid solutions containing nitric acid. Using a similar technique, polyantimonic acid has been deposited on silica gel.[27]

Two different procedures were suggested for depositing ammonium molybdophosphate (AMP) on silica gel. This sorbent was tested for separating radiocaesium from acid solutions.[28] TERADA et al.[29] also used silica gel as the support for AMP and some binary hexacyanoferrates used to concentrate radiocaesium from natural waters. In a similar way, GANZERLI et al.[30] used copper hexacyanoferrate deposited on silica gel to concentrate stable caesium from river and sea water.

In spite of the frequent use of silica gel as a support for inorganic ion-exchangers, it has not been used on a broader scale to treat liquid radioactive wastes. The procedure for decontaminating waste solutions from $^{137}$Cs proposed by WILDING[31] was based on the use of AMP precipitated "in situ" on silica gel. This product contained 23% (w/w) of AMP, and its sorption capacity was lower than that of a mixture of AMP with asbestos.

*Porous stainless steel membranes*[32] were used as support for hydrous titanium and zirconium oxides. $TiO_2$ and $ZrO_2$ were precipitated within the porous metal matrix using tetraisopropyl orthotitanate or zirconium propoxide and LiOH solution. Such stainless steel membranes might be impregnated with $TiO_2$ up to 7% of their weight. Impregnated steel membranes were tested as a means of removing radionuclides from the primary coolant used in pressurised water reactors.

*Organic polymers shaped as beads* have often been proposed as a support for inorganic ion-exchangers.[33-40] WATARI et al.[33] were the first to describe the preparation of copper hexacyanoferrate-loaded anion-exchange resin. Macroreticular anion-exchange resin (Amberlite IRA-904) was converted to the hexacyanoferrate form, and the different hexacyanoferrates were precipitated with solutions of the respective metals (Cu, Fe, Ni).[33,34] Harjula et al.[35] also studied possible applications of IRA-400 and IRA-904 anion-exchange resins and Chelex-100 chelating resin as supports for potassium-cobalt hexacyanoferrates. However, Harjula selected granular potassium-cobalt hexacyanoferrate for separating $^{137}$Cs from concentrates at the Loviisa NPP. For the preparation of AMP-bearing resin, Amberlite IRA-900 macroreticular anion-exchange resin has been used.[36] The resin retained 1.09 g AMP per gram of IRA-900.

Macroreticular anion-exchange resin AG-MP-1 (Bio-Rad) and Dowex MSA-1, type MP, were used by Dosh[37] to prepare resins loaded with sodium titanate, sodium niobate and sodium tantalate. Sodium titanate-loaded resins contained 30% to 40% (w/w) of sodium titanate in the dry residue. His studies proved that the sorption properties of sodium titanate are not influenced by the supporting material. Resins loaded with sodium titanate exhibited good mechanical stability, and a column filled with them was operated continuously for 527 hours with no evidence of particle attrition or channelling. Radiation stability of the loaded resin was shown to be good up to a dose of $5 \cdot 10^6$ Gy. Elution of spent resin and the possibility of its re-use were verified.

Other organic polymer beads were also employed as carriers for inorganic ion-exchangers. Dry beads were first soaked in an aqueous solution containing one component of the ion exchanger. After removing the supernatant, an aqueous solution of the second component was added to precipitate the inorganic ion-exchanger within the pores of the beads. Such a procedure was used to prepare a divinylbenzene-styrene copolymer loaded with AMP,[38] which was used to determine caesium in sea water. Macroreticular spherical cellulose was also proposed as a support for inorganic ion-exchangers.[39] Such cellulose loaded with nickel hexacyanoferrate[40] was tested as a means for separating $^{137}$Cs from liquid radioactive wastes in NPP A-1 (Slovak Republic).

Recently, granulated wood cellulose, cotton cellulose, and pine-wood sawdust were proposed as supporting matrices in a patented procedure for manufacturing sorbents with transition metal hexacyanoferrates.[41] The supporting material is treated with the suspension of freshly precipitated metal hexacyanoferrate and dried at 90 to 110 °C. The volume of inorganic ion-exchanger in the total volume of the produced sorbent is 1% to 30%. According to the authors, the suspension of transition metal hexacyanoferrate reacts with the surface of the supporting material. Due to this interaction, the resulting sorbents exhibit improved properties. The sorbents with granulated wood cellulose as a support are produced under the trademark "Fezhel", its varieties are produced as "Anfezh" and "Bifezh". All these sorbents are used for caesium separation.

*Fibrous polymers* as a support for inorganic ion-exchangers were first used by Krishnaswani et al,[42] who developed a procedure for impregnating acrylic fibres with iron hydroxide. Iron-treated fibres were used for the in situ extraction of various elements from sea water. Moore and Reid[43] developed a procedure for impregnating acrylic fibres (Monsanto "Acrilan", 3.0 denier, type B-16) with manganese oxides ($MnO + MnO_2$). Their procedure included the conversion of the fibre to a cation-exchange resin by treatment with 6M NaOH at 80 to 90 °C, and the sorption of manganese from 5M $MnCl_2$ at 30 to 40 °C and a pH of ~1 to 2. The manganese-soaked fibre was immersed in 6M NaOH at 25 °C to precipitate $Mn(OH)_2$, then separated, fluffed, and left exposed to air to oxidise $Mn(OH)_2$ to a mixture of hydrated MnO and $MnO_2$. As much as 12 to 15 g of manganese was loaded per 100 g of fibres. Subsequent washing removed less than 50% of the loaded manganese from the fibres. These alkali manganese-impregnated fibres have been used to extract radium and other trace metal from natural waters[43] and to remove radium from drinking water.[44]

Later on a simpler procedure was developed for preparing manganese-impregnated fibres (permanganate Mn-fiber.[45] Acrylic fibres were immersed in 0.5M potassium permanganate solution (at 70 to 80 °C), which partially oxidised the fibres and deposited $MnO_2$ on them. As much as 10 g of manganese could be loaded on 100 g of fibres. Loss of $MnO_2$ from these fibres during their use was less than 3%. These manganese fibres are suitable for extracting lead, mercury, copper, zinc, cobalt, and cadmium from dilute solutions.

Higuchi et al.[46] patented a procedure for preparing $MnO_2$, hexacyanoferrates, or their mixtures, supported by acrylic fibre in the form of woven or non-woven cloth. These materials may be used to collect and concentrate radionuclides and heavy metals present in liquid radioactive wastes, industrial waste waters, and natural water. The acrylic fibre element was prepared by copolymerising vinyl chloride with 8% (w/w) methyl acrylate. Such fibres will withstand up to 30% hydrochloric acid, nitric acid, or sulphuric acid. However, the resistance of these fibres to alkaline solutions is very low. The most suitable pH range for good performance of these materials is pH 7 to 9 with a near to 100% efficiency for collecting $^{54}$Mn, $^{65}$Zn, $^{59}$Fe, $^{60}$Co, $^{103+106}$Ru, $^{137}$Cs and $^{144}$Ce. The authors reported neither the quantities of inorganic ion-exchangers that can be supported by acrylic fibres nor the sorption capacities of their materials.

## Composite sorbents

Powdered and microcrystalline inorganic ion-exchangers may also be converted to granular form by using suitable binding materials. The required properties of such binding materials are the following: sufficient aggregation force, ample chemical stability, no adverse influence on the ion-exchange properties of the inorganic ion-exchanger, no ion-exchange properties of their own, high permeability for aqueous solutions of the targeted ions, and an ability to produce granules with a very high quantity of the active component of the absorber. Both inorganic and organic materials may be used as binding materials to prepare such composite sorbents.

### Composite sorbents with an inorganic binding matrix

The higher radiation and thermal stability of inorganic binding materials makes them attractive for preparing composite sorbents to be used to treat liquid radioactive wastes. Possible inorganic binding materials include e.g. appropriate *clay minerals*, which may be mixed with the powdered inorganic ion-exchanger and water to form a paste of suitable consistency. This paste is then used to form pellets, which are dried and calcined to improve their mechanical strength. Similar procedures are used by many commercial firms to prepare molecular sieves. However, in the production of some inorganic ion-exchangers, calcination at elevated temperatures is a disadvantageous step, because it may deteriorate the sorption capacity and ion-exchange kinetics of the material.

*Cement* also has been used as a binding material for granulating nickel hexacyanoferrate.[47] First a dry mixture of cement and hexacyanoferrate salt (3 : 2 or 4 : 1) was prepared and then mixed with water. The resulting dense grout was moulded into desired form. After 3–7 days of curing, the product was crushed and sieved. Granules obtained from both of these mixtures exhibited ample long-term stability in contact with solutions. The $K_D$ values for caesium from saline solutions (~20% solutions of sodium and potassium salts) ranged from 4000 to 8000.

An interesting procedure for granulating some inorganic ion-exchangers was proposed by PEETERS et al.[48] Barium sulphate and barium carbonate are usually obtained as fine powders, and as such are unsuitable for use in industrial columns. However, a suitable structure can be imparted by preparing $BaSO_4$ or $BaCO_3$ as a mixed precipitate with nickel hexacyanoferrate. This mixed precipitate is filtered (without washing), dried, and ground into granules of the required size.

Another suitable binding material is *silica gel.* A sol-gel procedure[49] is used for granulating powdered inorganic ion-exchangers into a matrix of $SiO_2$. Urea and hexamethylenetetramine are added to the sol of silicic acid and up to 70% (w/w) of exchanger. This mixture is dispersed into an organic medium, such as silicon oil, at elevated temperature. The spherical particles produced during dispersion must be purified from the residue of the organic dispersion medium before their use. A composite sorbent containing AMP prepared by this procedure[50] contained 65% (w/w) of the active component in the dried residue and had a sorption capacity of 0.22 mmole Cs · $ml^{-1}$. Although, by drying this sorbent partially decreased its ion-exchange kinetics, the sorption capacity of a packed bed increased from 0.10 mmole Cs · $ml^{-1}$ to 0.22 mmole Cs · $ml^{-1}$. Moreover, the sorbent was stable during twenty sorption-elution cycles or for 3 weeks of operation.

KRYLOV et al.[51] produced a silica gel matrix that contained higher loadings of the active component (when compared with the sol-gel procedure), which provided higher sorption capacity. Their laborious procedure included concentrating a dilute sol of silicic acid (prepared on cation exchangers) by evaporation to 28–32% (w/w) $SiO_2$. The finely divided active component of barium sulphate, activated by calcium, was added to this concentrated sol. The optimum ratio was found to be 7 g of $SiO_2$ to 100 g of $BaSO_4$. Pellets produced by pressing the resulting paste through defined openings were dried at 100 °C. Suitable granules were obtained by sieving the crushed pellets. Higher drying temperature adversely affected the properties of this material.

Internal gelation was used by COLLINS et al.[52,53] for the preparation of composite beads of *hydrated titanium or zirconium oxides* containing embedded sodium or potassium cobalt hexacyanoferrate. The basic procedure for the preparation of composite microspheres[53] is similar to that proposed by MELICHAR and TYMPL[23] for preparing spherical particles of pure inorganic ion-exchangers (see Fig. 2), the hexacyanoferrate salts are added in the form of a powder or a slurry to the initial solution of titanium or zirconium chloride.[53] As much as 32.1% of sodium cobalt hexacyanoferrate could be embedded into the binding matrix. For the use at lower pH values, the oxidic matrices could be converted to their respective phosphate forms. The resulting beads were structurally strong, no apparent degradation of microspheres was observed after 336 hours of contact with simulated liquid radioactive waste. They could be effectively used in the pH range 1 to 10.

Another suitable inorganic binding material is *alumina* ($Al_2O_3$). DOSH[37] studied the properties of sodium titanate pellets produced by the Norton Company (Akron, Ohio, USA). The pellets contained 10 to 30% of binder material and were dried using temperatures that ranged from ambient temperature to 340 °C. Pellets with satisfactory strength and strontium sorption capacity were produced by calcinating at 320 °C for 1 hour the mixtures containing 70% sodium titanate and 30% alumina.

The strength of pellets prepared with *calcium aluminate*,[37] another material used to prepare pellets of sodium titanate, was inferior to that of pellets containing alumina binder when both were dried at ambient temperature. Pellets with calcium aluminate binder were degraded by contact with caustic solutions.

### Composite sorbents with an organic binding matrix

The development of organic macromolecular materials whose properties may be modified to meet various requirements also resulted in their being used to granulate or to modify many powdered materials.[54–83] The classification of such materials is rather problematic because the literature (namely the patents) contain broad lists of polymers prepared and/or modified by many different procedures and because most of these polymers have rarely been used.

WHITE[54] proposed a broad scale of *hydrophilic gels* for granulating finely divided ion-exchange materials. In his procedure, he used water-soluble material that had been gelled in an aqueous medium to a water-insoluble form. Such gelable material may be a natural substance (gelatine, cellulose) or may be a synthetic gel formed by cross-linking polyacrylamide or polymethacrylamide. These synthetic gels may also be formed by polymerising water-soluble vinyl monomers in an aqueous medium containing a water-soluble cross-linking agent. Polyacrylamide gel was later used by Shigetomi et al.[55] to prepare gel particles containing various metal hydroxides. These sorbents were used to collect uranium from sea water. A disadvantage of gel-based sorbents is their relatively high water content (70% to 90%) and their poor stability in strong acid media.

Some of the *procedures of agglomerating suspended particles* patented by Rosenthal[56] may also be used to prepare composite sorbents. The granulating agent in this case is a synthetic plastic dissolved in a liquid organic solvent. Plastics that serve as granulating agents include polyacrylic acids, polymethacrylates and their copolymers, polyvinyl acetates, cellulose derivatives, polystyrene, polyamides, polycarbonates, etc.

To improve the granulometric properties of powdered ion-exchangers, *polymers slightly soluble in water* (such as polyvinyl alcohol) were used. Yoroda[57] mixed an aqueous solution of polyvinyl alcohol with natural bentonite and dried then pulverised the resulting paste. A disadvantage of this process is the slow dissolution of the organic binding polymer, especially at elevated temperatures.

*Non-hydrophilic binding agents* can be used if they are added in an amount just sufficient to bind the particles together, but not enough to prevent contact between the inorganic material and the solution. Stejskal et al.[58,59] used polyvinyl acetate, polystyrene, polyvinyl chloride, polymethyl methacrylate, and epoxy resin as binding material. The organic polymer was dissolved in a suitable organic solvent and mixed with a powdered sorbent to produce a paste that was dried, crushed and sieved. Ammonium molybdophosphate and zinc hexacyanoferrate were granulated in this way. A similar procedure[60] was also used to prepare granules of nickel hexacyanoferrate with polyvinyl chloride.

The preparation of composite ion-exchangers of hydrated oxides of titanium, zirconium or tin and a thermosetting resin (binding matrix) as an *epoxy, unsaturated polyester, or polyurethane* resin was described by Takeuchi et al.[61] The resulting composite sorbents are suitable for separating many anions (especially phosphate ions) and cations. They can be regenerated and used over a long period of time. These sorbents are prepared by directly mixing the powdered dry metal oxide hydrate (or their mixture) with a liquid resin or with a solution of the resin in a suitable organic solvent. The mixed components are cured at room temperature or at elevated temperatures up to 90 °C. The cured material is then crushed and sieved.

Singh and Theyunni[62] developed a procedure for preparing granules of ammonium molybdophosphate (AMP) with polyvinylbutyrale and epoxy resin. AMP powder was at first granulated with polyvinylbutyrale as a hydrophilic binder and then cured with the epoxy resin. The curing was carried out for ten hours at 80 °C and the resulting hard mass was pulverised and sieved to different size fractions. This composite ion-exchanger contains as much as 70% of AMP, and was proposed for separing caesium from acidic solutions. Chemical and mechanical stability of the sorbent in 3M $HNO_3$ is quite high, its stability is not adversely affected by a radiation dose of $10^4$ Gy.

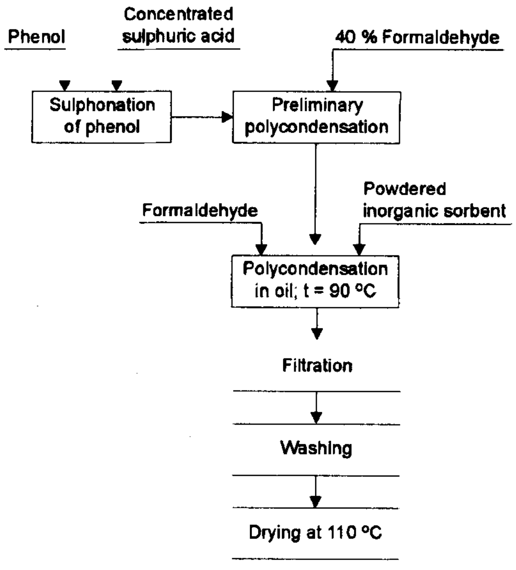

*Fig. 3.* Flow-chart for preparing composite ion-exchangers with phenolsulphonic-formaldehyde resin as the binder[68]

The procedure used to prepare macroreticular *spherical cellulose* from viscose[39] was also proposed for the preparation of composite absorbers. This procedure may be applied to inorganic ion-exchangers that are sufficiently stable in an aqueous alkaline solution of technical viscose cellulose. Composite sorbents containing PbS and $SiO_2$ were prepared by this method.

For stiffening biomasses containing the mycelia of micro-organisms (preparation of so called "biosorbents") a polymerisable component from the group consisting of *formaldehyde, resorcinol, urea, epoxide resin, acrylic resin*, etc. was found to be suitable.[63] The solid product is crushed and sieved. Such a material has good sorption properties for uranium and heavy metals. A similar procedure for stiffening biomasses of plant or algae material makes use of urea or urea with formaldehyde as binder.[64] The crushed and sieved product polymerised at 100 °C is suitable for separating uranium and heavy metals. An improved procedure[65] for stiffening the biomasses of mycelia fungi involves the dispersion of dry biomass in a non-polar organic medium, agglomeration of the dispersed biomass with a polymerising component, such as *formaldehyde, formaldehyde-resorcinol, formaldehyde-urea*, and a surface-active agent in a solvent immiscible with the dispersion medium. Stiffening of the agglomerated mixture is initiated by adding a catalyst and heating the mixture to at least 70 °C.

*Phenolic resin,*[66] were used to prepare spherical particles of composite absorbers with metal hydroxides as the active components. The phenolic resins are at first pre-condensated with an aldehyde compound in the presence of an acid catalyst. A metal salt or oxide is then incorporated into the reaction mixture. Salts of titanium, iron, aluminium, zirconium, tin, antimony, etc., may be used. A polycondensation reaction is completed while the resulting reaction mixture is suspended in a suitable medium, such as carbon tetrachloride, chloroform, or chlorbenzene at temperatures of 70 to 150 °C. After the reaction is complete, the resulting sorbent is removed from the reaction mixture and treated with an alkaline agent. Such sorbents can be used to purify various waste waters, including wastes from nuclear power plants.

*Phenolsulphonic-formaldehyde resins* were used by Narbutt et al.[67] to prepare composite ion-exchangers in the form of spherical beads. A flow diagram of the preparation[68] is shown in Fig. 3. The polycondensation process was also operated in a fluid reactor on a pilot plant scale. Composite sorbents containing the following active components have been prepared by this procedure: hexacyanoferrates of titanium(IV),[69–72] zinc,[68,69,73] nickel[68,69,73] copper[68] and cobalt,[69,72,74] as well as titanium phosphate,[96] synthetic mordenite,[69,72] and hydrated antimony pentoxide (polyantimonic acid).[69,75] Such composite sorbents typically contain 15% to 35% (w/w) of the active component in the dried residue,[68,72] with the exception of hydrated antimony pentoxide, which contains 60% of the inorganic filler.[69,75]

The mechanical stability of the composite beads of 1 mm diameter was 25–30 N.[72] A review of potential applications of these sorbents in nuclear and radioanalytical chemistry was recently published.[76] The phenolsulphonic-formaldehyde matrix is chemically stable in strongly acidic to slightly alkaline media, except for solutions containing oxidising agents such as 5 to 7M $HNO_3$ in which the matrix slowly degrades.[75,76] The phenolsulphonic-formaldehyde binder is not totally inert, as it behaves as a strong-acid cation exchanger.[69]

The described preparation procedure in unsuitable for active components that are unstable in sulphuric acid. Although these composite sorbents offer advantages for many potential nuclear applications,[76] their main disadvantage is rather slow ion-exchange kinetics in moderately to highly saline solutions.[70,72,74]

*A sulphonated polystyrene-divinylbenzene polymer*[77] was used to prepare composite sorbents containing hydrated antimony pentoxide as the active component. The prepared sorbent contained ~40% (w/w) of inorganic filler and was synthesised in a block polymerisation process from styrene, divinylbenzene, benzoyl peroxide and powdered (<0.03 mm) active component. The polymerisation product was swollen in dioxane and sulphonated. The final product was washed with distilled water, ground and sieved. This composite sorbent was used for separating sodium from digested biological material in concentrated $HNO_3$ solutions. However, the sorption capacity was lower than the theoretical value. Attempts to obtain a composite sorbent with a higher content of the active component were unsuccessful.

Hydrophilic *polyacrylic hydrazide (PAH)* was used for granulating hydrous titanium oxide.[78,79] Titanium oxide powder was homogenised with an aqueous solution of PAH and dried at 60 °C. The granular sorbent obtained by crushing the resulting solid, washing it with water, and sieving was used for the study of the rate of uranium sorption from sea water.

Polymers based on *polyacrylonitrile (PAN)* were also used as an organic binder for the preparation of composite sorbents[66,78,80–82] At first, modified PAN was used to prepare a composite sorbent for radium separation.[80] Later, an universal procedure was developed for preparing composite sorbents containing any inorganic ion-exchanger (active component).[81] The characteristics of these sorbents are given in the next chapter.

Japanese authors published several papers on the use of PAN as a binding polymer for granulating hydrous oxides of polyvalent metals, such as titanium oxide.[66,78,82] Nakamura et al.[82] used a commercial sorbent PAN-HTO (Asahi Chemical Industry Co., Ltd.) containing hydrous titanium oxide granulated with PAN to study the uptake of uranium from sea water. The results of scanning electron microscopic observation revealed that the particles were not homogeneous. A crust of PAN with many holes was observed, the pore size of the inner part of the particles was larger than that near the surface.

## Composite sorbents consisting of inorganic ion-exchangers and polyacrylonitrile binding matrix

Modified polyacrylonitrile was proposed as a universal binding polymer for almost any inorganic ion-exchanger (active component).[81] A flow-chart for preparing composite ion-exchangers containing modified PAN as the binding polymer is shown in Fig. 4.

This procedure can be modified or simplified in several ways. The initial components (or their solutions) for preparing the inorganic ion-exchanger can in some cases be mixed directly with the solution of the binding polymer, instead of using the ready made dried and powdered exchanger. The active component of the composite ion-exchanger is then formed during (or after) the coagulation of the binding polymer. Another possibility is to mix one of the components of the inorganic ion-exchanger with the solution of the binding polymer while the other component is dissolved in the coagulation bath.

These methods enable incorporation of very fine to colloidal particles of the active component in the binding polymer, which increases the capacity and improves the ion-exchange kinetics of the resulting sorbent. The final product can be shaped as grains, beads, fibres, felt, fabric, membranes, tubing, etc.

The use of PAN-based organic binding polymers has a number of advantages related to the relative ease with which

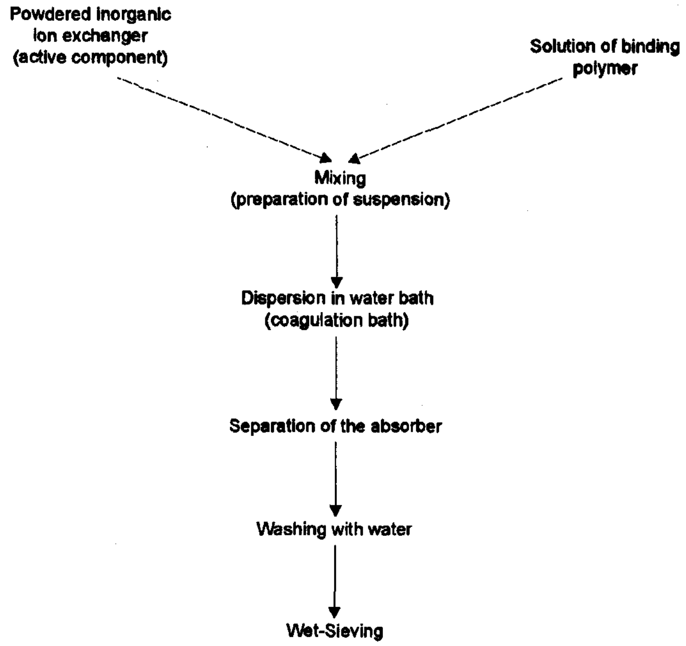

*Fig. 4.* Flow-chart for preparing composite ion-exchangers containing modified polyacrylonitrite (PAN) as the binder[83]

its physico-chemical properties (hydrophilicity, porosity, mechanical strength) are modified. These properties can be modified by the degree of polymer cross-linking, the use of suitable co-polymers, or by the composition and temperature of the coagulation bath. Another advantage is the ability to prepare the composite ion-exchangers directly in the aqueous solution, eliminating the necessity of introducing organic water-immiscible solvents and oils, used frequently in other technologies, that would require subsequent removal by washing.

### *Chemical and radiation stability of PAN-based composite sorbents*

A PAN binding polymer is stable in all aqueous solutions of common electrolytes, except concentrated solutions of $ZnCl_2$, LiBr, $CaCl_2$ and NaSCN, which are known to dissolve polyacrylonitrile. This polymer also dissolves in acids more concentrated than 8M $HNO_3$, 5M $H_3PO_4$, or 5M $H_2SO_4$.

*The chemical stability* of the PAN binder is excellent in neutral to weakly acid solutions. In acid media with a pH of 0, and in alkaline media with pH up to 13, no deterioration of the sorption properties of composite sorbents was observed during several weeks of application[83–88] at temperatures below 25 °C.

In alkaline solutions at $pH > 13$, chemical stability of PAN is negatively affected by its hydrolysis. The influence of the hydrolysis increases with increasing pH and temperature. The binding polymer subsequently hydrolyses to gel, becomes hydrophilic, and finally dissolves. The hydrolysis itself does not deteriorate the sorption properties of composite sorbents, it affects only their mechanical stability.

Chemical stability of PAN in 1M NaOH + 1M $NaNO_3$ solution was found to be sufficient for applications of composite sorbents not extending over 10 days at ambient temperature.[87,88] Because of the high sorption rate achievable with most PAN-based composite sorbents, their sorption capacity will usually be exhausted earlier. Moreover, most active components (inorganic ion-exchangers) themselves are chemically not sufficiently stable in media with high alkalinity.[89] Thus the stability of PAN binder in alkaline solution, even though limited, is sufficient for most of the practical applications.

*The radiation stability* of composite exchangers will depend on the radiation stability of both the inorganic active component and the binding organic matrix (which will in most cases be the limiting factor). The radiation stability of the PAN binder was found to be satisfactory up to radiation doses of $10^6$ Gy, when irradiated in distilled water or 1M $HNO_3$ + 1M $NaNO_3$. The sorption properties of AMP-PAN composite sorbent (ammonium molybdophosphate active component) were not negatively affected by this radion dose.[87,88] At higher doses, only some hardening and higher fragility of the polymer was observed. This effect was ascribed to PAN polymer cross-linking during irradiation.[88]

In alkaline solutions two effects are combined because higher radiation doses require relatively long irradiation time. Therefore, in addition to the influence of radiation, influence of chemical stability has to be considered. In this case, the radiation induced cross-linking of the polymer positively affects its chemical stability.[88]

In a pilot plant verification of the technology proposed for decreasing the activity of the LTFSP water at NPP A-1 at Laslovské Bohunice, Slovak Republic,[83] the radiation stability of the NiFC-PAN composite sorbent (nickel hexacyanoferrate active component) was confirmed to be sufficient for practical applications.

### *Prospective applications of PAN-based composite sorbents*

The procedure for producing composite sorbents can be applied on most of the inorganic ion-exchangers known. The list of the composite ion-exchangers produced until now is shown in Table 1.

The produced sorbents are preferably stored swollen without drying, the swollen beads contain typically ~ 60% (w/w) of water. The contents of active component in composite exchangers can be varied over a very broad range (5–95% of the dry weight of the composite ion exchanger) depending on the application foreseen. Even composite sorbents containing mixtures of various active components may be prepared by the mentioned procedure. The properties of such sorbents can thus be "tailored" to the special features of the application. PAN binding matrix does not influence the possibility to regenerate the composite sorbents such possibility is determined solely by the nature of the respective active component.

The kinetics of ion exchange on the PAN-based composite ion-exchangers is rapid. As a consequence of the fact, that the active component is usually embedded into the binding matrix in the form of finely divided particles, the sorption kinetics (and/or sorption capacity) on composite sorbents is substantially faster (larger) than that measured on the pure active component with grain size similar to that of the composite sorbent used. Typically, flow rates 50–100 BV · hour$^{-1}$ (BV – column bed volume) are used,[83–85,89,91] the decontamination factors at these flow rates reach values of $D_f = 10^2$–$10^3$. The sorption properties of these composite sorbents are not negatively influenced by high salinity.[88,89,91]

Many potential *technological applications* of composite sorbents were tested during the last several years, some of them were reported or reviewed in recent papers.[83–86,89–91] Marsh et al.[92–97] evaluated the performance of 17 types of PAN-based composite sorbents for the treatment of U.S. DOE liquid radioactive wastes. The results of their tests indicate numerous prospective areas for applications.

Five types of the most promising composite sorbents were also tested within the Novel Absorber Evaluation Club (operated by AEA Technology, Harwell Laboratory, U.K.), using the reference waste stream NAEC S1 at pH ~ 9. Results of the sorption of 12 elements on the composite sorbents were reported.[98]

*Table 1.* PAN-based composite sorbents

| CODE | Inorganic ion-exchanger |
|---|---|
| AMP-PAN | Ammonium molybdophosphate |
| NiFC-PAN | Nickel hexacyanoferrate |
| KNiFC-PAN | Potassium-nickel hexacyanoferrate |
| CoFC-PAN | Cobalt hexacyanoferrate |
| KCoFC-PAN | Potassium-cobalt hexacyanoferrate |
| ZrP-PAN | Zirconium phosphate |
| TiP-PAN | Titanium phosphate |
| MnO-PAN | Manganese dioxide |
| TiO-PAN | Titanium oxide |
| ZrO-PAN | Zirconium oxide |
| MgO-PAN | Magnesium oxide |
| NM-PAN | Manganese dioxide and nickel hexacyanoferrate |
| ZrOP-PAN | Zirconium oxide and zirconium phosphate |
| NaTiO-PAN | Sodium titanate |
| CSbA-PAN | Crystalline antimonic acid |
| SnSbA-PAN | Tin(IV) antimonate |
| TiSbA-PAN | Titanium(IV) antimonate |
| TS60-PAN | Sodium titanosilicate |
| Ba[Ca]$SO_4$-PAN | Barium sulphate activated by calcium |
| CuS-PAN | Copper sulphide |
| Na-Y-PAN | Synthetic zeolite Na-Y |
| M315-PAN | Synthetic mordenite M315 |
| CLIN-PAN | Natural clinoptilolite |
| HPM-PAN | Sr- and Ra-selective ternary ion-exchangers |
| CAPM-PAN | |

Examples of application of composite sorbents in concentration and separation steps of various *analytical procedures* were reviewed recently,[86] among the most important ones the following can be listed:

The procedure for large-volume concentration of caesium from surface water was used on a routine basis for the monitoring of NPP sites[99] and for the determination of migration forms of $^{137}$Cs.[99,100] After the Chernobyl accident it has been used for monitoring of drinking water contamination and for determination of contamination of sea water. The procedure enables concentration of caesium from up to 100 l of surface water in less than 4 hours.[101]

Concentration and separation of caesium on NiFC-PAN sorbent from urea and milk is used on a routine basis in the Czech Public Health control system.

Concentration of radiocobalt was developed for drinking water and successfully tested for river water, too.[100]

The research and development in the field of composite sorbents consisting of inorganic ion-exchangers and polyacrylonitrile binding matrix is currently directed towards developing additional types of composite sorbents with new prospective active components, testing their sorption properties, and their prospective application. Attention is also being paid to the options for solidifying the spent composite sorbents for their final disposal and to the study of radiation stability of both the sorbents and their solidified products.

*

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