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Evaluation of Polyacrylonitrile (PAN) as a Binding Polymer for Absorbers Used to Treat Liquid Radioactive Wastes

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ABSTRACT

The chemical and radiation stability of polyacrylonitrile (PAN) in the form of beads (B-PAN), similar to the beads of composite absorbers, and one selected composite absorber (ammonium molybdophosphate, the active component in PAN binder [AMP-PAN], a prospective candidate for the treatment of acidic wastes) were studied. Aqueous 1M HNO_3 + 1M $NaNO_3$, 1M NaOH + 1M $NaNO_3$, and 1M NaOH were chosen as simulants of DOE acidic and alkaline wastes. In addition, radiation stability was determined in distilled water. The chemical stability of B-PAN and AMP-PAN beads was tested for a period up to one month of contact with the solution at ambient temperature. The radiation stability of the beads was checked in a radiation dose range $10^3 – 10^6$ Gy ($10^5 – 10^8$ rads).

In acidic solutions the stability of PAN binder was proved not to be limited by either chemical or radiation decomposition. PAN binder may thus be used for preparing composite absorbers for treatment of acid wastes from DOE facilities. The same conclusion is valid for alkaline solutions with pH up to 13.

In highly alkaline solutions (concentration of NaOH higher than 1 M) and in the presence of $NaNO_3$, the stability of the tested polyacrylonitrile polymer was sufficient for applications not extending over 10 days. Cross-linking of the polymer caused by ionizing radiation was found to have a positive influence on chemical stability. This effect enables a longer period of applicability of PAN-based composite absorbers. Because of the high sorption rate achievable with PAN-based absorbers, the stability achieved is sufficient for most applications in the DOE complex. The chemical stability of binding polymer may also be further improved by testing another, more suitable type of polymer from the broad family of polyacrylonitrile polymers.

Acknowledgments

This research project was managed by Sandia National Laboratories under DOE Technical Task Plan (TTP) AL-234302, International Efficient Separations. This task was funded and pursued under the direction of Dr. Teresa B. Fryberger, Program Manager, DOE/EM-53. The Principal Investigator was Rudolph V. Matalucci, formerly of the Sandia International Programs Department 6907.

The technical and programmatic support efforts by the Institute for Central and Eastern European Cooperative Environmental Research (ICEECER) at Florida State University (FSU), Tallahassee, Florida, under Sandia Contract AE-4761, are acknowledged. More specifically, the technical liaison and subcontract support provided by John E. Moerlins and Roy C. Herndon from the ICEECER are gratefully appreciated. This work was accomplished by the Czech Technical University (CTU) in Prague, Czech Republic, via an Agreement for Services between FSU and CTU.

The technical guidance, suggestions, and significant contributions made by Norman E. Brown and S. Fredric Marsh of the Sandia Environmental Technology Department 6624 are also appreciated. Their technical guidance, especially during the planning and execution of the experimental work, was valuable for the successful progress made by this project.

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Preface

The text for this report was provided in English by the authors at the Czech Technical University (CTU). Minor editing was accomplished at Sandia to clarify technical terminology without attempting to modify the content as established by the authors.

This report describes the first phase of a two-phase experimental effort that was accomplished at CTU under a service agreement through a Sandia National Laboratories contract with Florida State University.

1.0 INTRODUCTION

Composite inorganic-organic absorbers represent a group of inorganic ion-exchangers modified by using binding organic material to produce larger sized particles having higher granular strength. Such modification of these originally powdered or microcrystalline inorganic ion-exchangers makes their application in packed beds possible.

Modified polyacrylonitrile (PAN) has been proposed as a universal binding polymer for practically any inorganic ion-exchanger (active component).[1,2] The principal preparation scheme of composite ion exchangers containing modified PAN was presented by Šebesta et al.[3] The method developed enables preparation of granular absorbers even from inorganic ion-exchangers that are impossible or very difficult to synthesize in granular form.

The use of PAN-based organic binding polymer has a number of advantages provided by the relatively easy modification of its physico-chemical properties (hydrophilicity, porosity, mechanical strength). The ion exchange kinetics and sorption capacity of such composite ion exchangers are not influenced by the PAN binding polymer. The contents of the active component in the composite exchanger can be varied over a very broad range (5 – 95% of the dry weight of the composite ion exchanger), depending on the planned application.

The proposed method can be applied to most known inorganic ion exchangers. A list of the composite ion exchangers already produced in our laboratory is shown in Table 1. Their properties depend mainly on the properties of the active component. Some of the absorbers can be regenerated (e.g., AMP-PAN, TiO-PAN, NaTiO-PAN), and some cannot (e.g., ferrocyanides of transition metals—NiFC-PAN, CoFC-PAN). The possibility of regenerating composite absorbers is governed solely by the nature and properties of their active components. The proposed procedure enables preparation of composite absorbers containing mixtures of various active components in desired ratios. The properties of such a composite absorber can thus be exactly "tailored" to the specific features of the foreseen application.

These composite absorbers were proposed and tested for separating and concentrating various contaminants from aqueous solutions. Their high selectivity and sorption efficiency are advantageous for the treatment of various radioactive and/or industrial waste waters, removal of natural and/or artificial radionuclides and heavy or toxic metals from underground water (plumes), and determination of radionuclides (^{137}Cs, ^{60}Co, U, Ra) in the environment. Examples of some of these applications and some possible prospective applications are reviewed in several recent papers and reports.[3-8]

Early in 1993 a first set of a few composite absorbers was submitted for testing to one of the U.S. Department of Energy (DOE) national laboratories. S.F. Marsh of Los Alamos National Laboratory (LANL) included these materials in his screening studies of prospective absorbers for treatment of DOE liquid radioactive wastes. As a result of this first contact, a Memorandum of Understanding was approved between LANL and the Czech Technical University in Prague (CTU), and a small contract was placed with CTU to help support its program to develop and prepare new composite absorbers. An initial review of composite absorber technology was performed under this contract and published as a LANL report.[9] Thus far, some 20 composite absorbers have been submitted to LANL for evaluation, many of them prepared specifically for DOE needs. These absorbers were tested extensively with DOE radioactive waste simulants in LANL absorber screening studies and the tests revealed that "many have shown outstanding performance."[10] The results of these studies were published in several recent LANL reports.[11-14] Ammonium molybdophosphate (AMP) -PAN composite absorber is currently being tested at Idaho National Engineering Laboratory (INEL) for possible application to the removal of ^{137}Cs from acidic high level waste.

Table 1. PAN-based Composite Absorbers

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
Ba[Ca]SO_4-PAN	Barium sulfate activated by calcium
CuS-PAN	Copper sulfide
Na-Y-PAN	Synthetic zeolite Na-Y
M315-PAN	Synthetic mordenite M315
CLIN-PAN	Natural clinoptilolite
HPM-PAN CAPM-PAN	Sr- and Ra-selective ternary ion-exchangers

Initial contacts with Florida State University (FSU) were established in the spring of 1993 during a visit by J.E. Moerlins of FSU to Prague. A project was proposed by Sandia National Laboratories in January and February 1994 to demonstrate the performance of composite absorbers with polyacrylonitrile binder at one of the DOE sites using an actual waste stream. During the discussion of possible waste streams for such a demonstration, a question was raised about the chemical and radiation stability of the polyacrylonitrile binder in the extremely harsh conditions typical of many of the DOE high-level waste streams (high concentrations of acids or alkalis, high salinity—Hanford, INEL, or Oak Ridge National Laboratory type wastes). This question was not readily answerable because of

- a lack of previous experience with the application of composite absorbers for treatment of such waste streams and
- a lack of relevant data in the literature about the behavior of polyacrylonitrile under similar conditions.

Thus the focus of this study was changed from a demonstration of the performance of the absorbers to an evaluation of PAN as a binding polymer for absorbers used to treat liquid radioactive wastes. CTU was contracted by FSU to perform this study under Agreement for Services No. FSU/CTU-1; the contract is co-managed by Sandia National Laboratories (SNL) under the guidance of R. Matalucci. Originally the agreement was intended to include the period between 25 July 1994 and 31 March 1995. During a meeting of the participants with DOE Headquarters personnel (T. Fryberger, EM-53) and SNL representatives in Budapest, Hungary at the BUDAPEST'94 conference (22 September 1994), the parties agreed to extend the period of the project up to 12 months. The experimental program of the project (defined originally in the agreement) was modified and agreed on.[10]

The final agreement delineates a two-phase project. Phase I should establish and demonstrate the stability of PAN in acidic and alkaline solutions using actual performance data of this polymer with or without absorbers. This phase of the effort should evaluate the chemical and radiation stability of PAN using laboratory techniques, and produce a draft report summarizing the results. Phase II should establish and demonstrate the performance of the PAN material using a designated PAN/absorber combination and the results from Phase I for separations of either simulated or actual radioactive liquid waste. A technical review and resolution process at the completion of Phase I are required before laboratory testing will proceed to Phase II. The final Phase I experimental program is as follows:[10]

A. *Testing Techniques to Measure Physico-Chemical Properties of PAN Beads and Composite Absorbers.*

Selected materials should be contacted with specified liquids for periods of 1, 3, 7, 14, and 30 days with continuous shaking. Materials selected include pure PAN beads and AMP-PAN composite absorber. Specified liquids include 1 M HNO_3 + 1 M $NaNO_3$ for testing both pure PAN beads and AMP-PAN, whereas 1 M NaOH and 1 M NaOH + 1 M $NaNO_3$ solutions were selected for testing pure PAN beads. Testing procedures were established to include (1) total bead volume measurement, (2) swelling, (3) microscopic examination, and (4) wet sieving for all the materials tested. In addition, changes in sorption capacity and kinetics should be determined for AMP-PAN.

B. Evaluation of Chemical Stability of PAN.

The experimenters agreed to conduct a review of literature data on the physical and chemical properties of PAN. The selection of testing conditions is given in Part A.

C. Evaluation of Radiation Stability

Irradiation experiments were determined to consist of AMP-PAN in 1 M HNO_3 + 1 M $NaNO_3$ and pure PAN beads in water. Radiation levels up to the maximum of 10^6 Gy (10^8 rads [Gy = 100 rads]) were agreed on. Testing conditions should be the same as given in Part A.

D. Preparation of Technical Report

Because of CTU's ability to produce only a limited number of bound reports, the participants agreed to provide the technical report also in an electronic format.

The present report is the Draft Phase I Report—the first deliverable due under Agreement for Services No. FSU/CTU-1. As required by the agreement, this report summarizes laboratory and analytical data and contains a discussion of the results, conclusions, and recommendations for proceeding to the next phase.

2.0 REVIEW OF DATA ON PHYSICAL AND CHEMICAL PROPERTIES OF PAN

2.1. Introduction

The review of data on the physical and chemical properties of PAN was performed as an introductory step in the study of chemical and radiation stability of PAN. The intent of this review was not to gather an exhaustive set of data, but to provide general information on PAN and its copolymers, its physical and chemical properties, methods of preparation and production, and fields of application. More thorough attention is given to the radiation and chemical stability of PAN, namely its behavior under hydrolysis.

The information collected covers the properties of PAN and other copolymers of PAN, namely polyacrylonitrile fibers. Concerning its chemical and radiation stability, the properties of modified PAN as used for the preparation of composite absorbers are not expected to differ substantially from those of standard spun fibers.

Most of the information published on the chemical stability of PAN relates to its hydrolysis in homogeneous systems—solutions of PAN. Data on radiation stability relate mostly to properties of spun fibers, i.e., irradiation of dry material. Therefore it is difficult to draw any exact conclusions from these data for the modified PAN used for preparing the composite absorbers that will be subjected to the harsh chemical environment of heterogeneous systems and irradiated in a column bed (swollen). These data may only be used best to estimate general qualitative trends; quantitative information must be obtained experimentally.

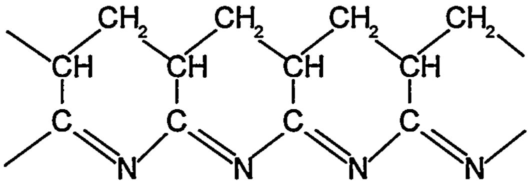
2.2. General Physical and Chemical Properties

The starting material for the manufacture of PAN, acrylonitrile, $CH_2{=}CHCN$, is now most frequently produced by one-step ammooxidation of propylene in the presence of catalysts, such as bismuth phosphomolybdates. This simple and cheap process for synthesizing the monomer led to decreased production costs in the 1960s and to a pronounced growth in its production.

Acrylonitrile polymers are manufactured by a radical polymerization of acrylonitrile initiated by peroxides or redox systems at temperatures below 100^0C, most frequently at $20 - 60^0$C. Typical polymers of acrylonitrile possess average molecular weights of 40,000 – 60,000. The acrylonitrile homopolymer is seldom used in practice. Of the acrylonitrile copolymers, the most common are polyacrylonitrile fibers, followed by copolymers with styrene (SAN), which are used in ABS polymers (composites, SAN-polybutadiene), and copolymers with butadiene (nitrile rubbers).

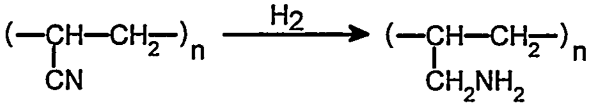
PAN differs in many respects from common commercial polymers. Typical properties of PAN are its hardness; stiffness; resistance to most solvents and chemicals; resistance to sunlight, heat, and microorganisms; slowness to burn and char; compatibility with polar substances; orientation ability; and low permeability to gases.

These unique properties are caused by the presence of nitrile groups in the polymer molecules and the resulting highly polar character of acrylonitrile polymers. On the other hand, polar nitrile groups cause an enhanced ability to interact chemically with the environment. PAN forms hydrogen bonds, transition metal ion complexes, donor-acceptor complexes, and undergoes a number of chemical transformations as well. Even the physical properties of PAN, such as its structure and morphology, are predominantly determined by the interactions of nitrile groups. The acrylonitrile homopolymer consists of crystalline (~50%), quasicrystalline, and amorphous phases. When heated it decomposes without melting; during decomposition it turns yellow, red, and finally black. The black product contains a conjugated double bond system (ladder polymer).



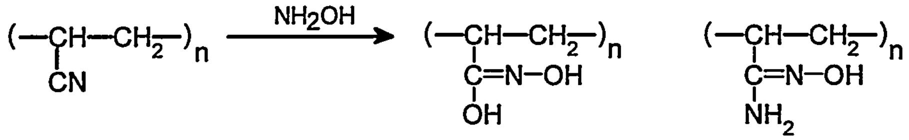
PAN only dissolves in (1) aprotic polar organic solvents such as dimethylformamide, dimethylacetamide, dimethyl sulfoxide, sulfolane, ethylene carbonate, and N-methylpyrrolidone, (2) concentrated sulfuric acid and nitric acid, and (3) concentrated aqueous solutions of some inorganic salts such as lithium bromide, sodium thiocyanate, and zinc chloride. Acrylonitrile copolymers are often soluble in less-polar organic solvents such as dioxane, tetrahydrofuran, chlorobenzene, cyclohexanone, and acetone.

Because of the presence of nitrile groups and alpha hydrogen atoms in PAN, the polymer undergoes a number of chemical transformations. It yields primary polyamine by hydrogenation,



$$(-\underset{CN}{CH}-CH_2-)_n \xrightarrow{H_2} (-\underset{CH_2NH_2}{CH}-CH_2-)_n$$

poly(hydroxamic acid) and poly(amidoxime) with hydroxylamine,



$$(-\underset{CN}{CH}-CH_2-)_n \xrightarrow{NH_2OH} (-\underset{\underset{OH}{C=N-OH}}{CH}-CH_2-)_n \quad (-\underset{\underset{NH_2}{C=N-OH}}{CH}-CH_2-)_n$$

and polyacrylic acid by alkaline hydrolysis (see below). The action of peroxides or ionizing radiation leads to the abstraction of alpha hydrogen atoms and the formation of polymer radicals, which participate in consecutive reactions such as crosslinking or grafting.

2.3. Polyacrylonitrile Fibers

The most widespread polymers of acrylonitrile are polyacrylonitrile fibers, called also acrylic fibers. The annual world production of PAN fibers was about two million tons at the beginning of the 1980s.

PAN fibers are classified into two groups according to the contents of acrylonitrile units: (1) the acrylic fibers proper, with a content of at least 85% monomeric units; and (2) modified acrylic fibers, also called modacrylic fibers, with a content of 35 – 85% acrylonitrile units. The most widely used comonomers are vinyl halogenides such as vinyl chloride, vinylidene chloride, and vinyl bromide, which impart low flammability to fibers and fabrics made from them. Also used are some other comonomers such as methyl acrylate, vinyl acetate, and ionic comonomers containing sulfo groups.

In industry, acrylonitrile is usually polymerized in aqueous dispersions using a redox initiator (most frequently a peroxysulfate/sulfite system with Fe(III)/Fe(II) catalysis). The polymerization is performed continuously in a stirred reactor. The product is an aqueous suspension of polymer particles. Also quite common is "solution polymerization," when the formed polymer remains dissolved in the solvent used. Some organic solvents (dimethylformamide, dimethyl sulfoxide) or concentrated aqueous solutions of some inorganic salts are used for this process. The advantage of solution polymerization is the possibility of directly using the formed polymer solution for spinning (see below). Emulsion polymerization of acrylonitrile is only rarely used in industry.

Acrylonitrile and modacrylic fibers cannot be spun from the melt because acrylonitrile polymers decompose on heating without melting. Hence their solutions are spun either by wet spinning, where the solutions are pressed into a precipitation bath containing non-solvents of PAN, or by dry spinning, where coagulation occurs in a stream of hot gas by solvent evaporation. Acrylonitrile fibers are produced predominantly as rayon.

PAN fibers exhibit a number of advantageous properties that predestine them for use in the textile industry. Here, only those properties will be mentioned that may be important for their other uses. PAN fibers are light: acrylic fibers have a density of 1.12 – 1.19 and modacrylic fibers have a density of 1.28 – 1.37. They are very resistant to chemicals and comparatively hydrophilic (water content 1.5 – 3.5%). Dilute inorganic acids and bases do not attack them; they dissolve in concentrated sulfuric acid and nitric acid. Although PAN fibers are degraded by hot concentrated alkalis, they are resistant to common organic solvents and oxidizing and reducing agents.

2.4. Radiation Stability of PAN

The effects of ionizing radiation on polymeric solids are widely studied because polymers often exhibit remarkable changes in their physico-chemical properties when irradiated even at low absorbed doses. The most important processes that occur during the irradiation are the following:

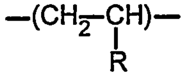
a) Creation of bonds between linear macromolecules of the polymer, called "crosslinking."

b) Breaking of the basic carbon chain that yields compounds of a lower molecular weight, called "scission" of a polymer (also referred to as "degradation").

c) Both processes (a) and (b) are accompanied by an evolution of various gaseous products.

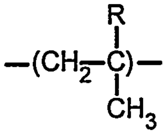
To describe these phenomena quantitatively, the following radiation-chemical yields (G-values, mol.J^{-1}) are widely used: G(c) = G(crosslinking), G(d) = G(degradation) and G(g) = G (gaseous product). Their values provide, in the same order, the **number of moles** (1) of crosslinked bonds, (2) of carbon chain breakdowns, and (3) of gaseous products **per Joule of absorbed radiative energy.**

Degradation and crosslinking processes usually compete during irradiation, and the final result depends on many other factors such as total absorbed dose, type of radiation used, etc. Polymers with G(c) > 4 G(d) undergo primarily crosslinking and the others undergo primarily scission. An empirical rule[15] states that polymers of elementary structural units, e.g.,



$$-(\mathrm{CH_2}-\underset{\mathrm{R}}{\underset{|}{\mathrm{CH}}})-$$

(where R stands for a radical) tend to crosslink rather than to degrade. Polymers of elementary units, e.g.,



$$-(\mathrm{CH_2}-\overset{\mathrm{R}}{\overset{|}{\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{C}}}}})-$$

undergo predominantly degradation. There are exceptions to this rule, of course.

Many experimental data and general rules on the radiolysis of various polymers are given in monographs.[16,17] However, the data on PAN radiolysis are scanty and sometimes controversial. Some authors consider PAN to be primarily crosslinking,[16] whereas others regard it as primarily degrading.[18] One author observed a "certain degree of crosslinking during the irradiation at lower absorbed doses"[19] even in the presence of oxygen—in spite of the fact that, as Swallow reports, the presence of oxygen supports degradation of the polymer and suppresses its crosslinking.[16] These apparent discrepancies are likely caused by differences in irradiation conditions, which lead to differences in the extent of oxidation. Under inert atmosphere, or under air at high dose rate, oxidation is minimal. For irradiation under air at low dose rates, however, extensive oxidation resulting in chain scission reactions may be the dominant mechanism. The results of the most recent studies seem to prove that PAN belongs among the predominantly crosslinking polymers.[20-22]

Irradiation of PAN, either by gamma radiation[20,21] or X-rays, promotes the abstraction of hydrogen atoms from PAN molecules, thus yielding hydrocarbon radicals with uncoupled electrons located on carbon atoms. Recombination of these radicals yields *C-C* bonds that are mainly responsible for the crosslinking of PAN. The other way to crosslink via nitrile groups comes into consideration:[21] Polymer radicals also add to the nitrile groups, and the resulting nitrogen radicals then initiate polymerization of the nitrile groups, leading to a polyene ladder structure.

No significant differences between the action of both types of radiation were observed. This can be readily understood by knowing that the radiative energy is being imparted to the absorber through a cascading electron displacement process, so that the series of ionizing sites formed has little dependence on the nature of the initiating ionization event. This lack of dependence on radiation type is commonly observed in radiation chemistry. Similar results can be expected from irradiation with beta particles and/or fast electrons, as their Linear Energy Transfer (LET) values approximate those of gamma radiation. The situation may become more complicated when radiation with higher LET (alpha particles for instance) is applied.

Gaseous products of radiolysis.[16,17] Hydrogen is the most abundant gaseous product that results from the radiolysis of polymers. Gaseous hydrocarbons of lower molecular weight are also formed, but to a lesser extent. Halogen-containing polymers yield the corresponding hydrogen halide. Table 2 summarizes the **total** G(g) values for various polymers as reported by Swallow.[16] The G(g) values were estimated at total absorbed dose of 1 MGy. Letters attached to G(g) denote either degrading (d) or crosslinking (c) polymers.[16,17,23]

Table 2. Total Radiation-Chemical Yields of Gaseous Production—G(g)[16]

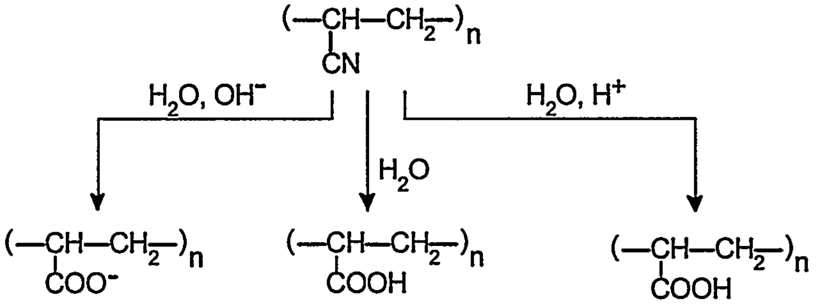
Polymer	$G(g).10^8$ [$mol.J^{-1}$]	Polymer	$G(g).10^8$ [$mol.J^{-1}$]
polytetrafluorethylene	0.528^d	polyisobutylene	7.67^d
polystyrene	0.715	polyvinylalcohol	9.95
polybutadiene	2.38	polymethylmethacrylate	11.5^d
polyacrylonitrile	3.42^c	polyethylene	21.0^c
natural rubber	4.56^c	polymethylacrylate	29.9^c

d - *"primarily degrading"*
c - *"primarily crosslinking"*

According to published data,[19] an absorbed dose of 100 kGy does not deteriorate the properties of polyacrylonitrile fibers and thus can be applied for radiation sterilization of polyacrylonitrile textiles. This value is obviously conservative to prevent undesirable coloration changes that are known to occur at significantly lower doses than the doses that change mechanical properties.[16,17]

2.5. Chemical Stability of PAN

The most important chemical characteristic of PAN relative to this project is its hydrolyzability. PAN can be hydrolyzed in both the presence of bases or acids and in neutral media.



Alkaline hydrolysis of PAN occurs readily by the action of aqueous potassium or sodium hydroxide in homogeneous media, e.g., a solution of PAN in dimethylformamide, dimethyl sulfoxide, dimethylacetamide solutions, or in concentrated aqueous solutions of sodium thiocyanate. Under these conditions, moderate temperatures (30 – 50°C) are sufficient for hydrolysis to occur. Apparently, higher temperatures and higher concentrations of alkaline hydroxide accelerate the reaction. In these cases, the nitrile groups transform into carboxamides and further into carboxylates; hence the final product is polyacrylic acid.[24]

Under hydrolysis conditions, the nitrile groups polymerize to some extent to azapolyenes -$(C{=}N)_n$, which finally also hydrolyze to carboxylates. Transient formation of conjugated azapolyenes is accompanied by strong coloration of the reaction mixtures, from yellow to dark red. Parallel reactions during hydrolysis result in a slow degradation of PAN, manifested by decreases in its molecular weight.[25]

At first the alkaline hydrolysis is slow, but it accelerates because of the formation of carboxylates on the polymer chain.[26,27] The participation of neighboring carboxylate groups in the hydrolysis is corroborated by the fact that copolymers of acrylonitrile with acrylic acid, methyl acrylate, or vinyl acetate (which contain carboxylates or from which they are readily formed) are hydrolyzed much faster than acrylonitrile homopolymers.[28] At higher degrees of hydrolysis, when the polymer already contains large numbers of carboxylate groups, the hydrolysis is again slower. The reason is the more difficult access of hydroxyl anions to the negatively charged polymer molecules, a result of electrostatic repulsion.

Acid hydrolysis of PAN, i.e., hydrolysis by aqueous mineral acids, also occurs comparatively easily. Commonly used are 60 – 90% sulfuric acid[29] or 65% nitric acid.[30] In mild conditions, at laboratory temperatures or lower, the hydrolysis of nitriles leads to amides and cyclic imides. At higher temperatures (90^0C) the final hydrolytic product is poly(acrylic acid).

Also during acid hydrolysis of PAN, an accelerating effect of carboxyl and carboxamide groups in the polymer chain on the hydrolysis of nitrile groups is observed.[29] In those acrylonitrile copolymers where the nitrile groups are mostly isolated, the hydrolysis is generally slower, depending also on the type of comonomer.[31]

Neutral hydrolysis, i.e., hydrolysis by water, in the absence of low-molecular-weight acids or bases, starts at temperatures above 160^0C and proceeds at a reasonable rate only at 180 – 210^0C. The hydrolysis is at first very slow. The polymerization of nitrile groups predominates, leading to colored azapolyenes. In the next accelerated step, the polyenes are hydrolyzed to produce amides, which in turn hydrolyze to carboxyl groups. The final product is a polymer containing (besides carboxyl groups) a considerable amount of carboxamide groups. Also, the presence of carboxyl groups in the polymer chain catalyzes the hydrolysis of nitrile groups.[32,33]

The hydrolysis of PAN by aqueous solutions of ammonium carbonate, ammonium hydrogen carbonate, or urea at 220^0C proceeds similarly.[34] However, hydrolysis at these high temperatures is accompanied by degradation of the polymer, leading to a decrease in its molecular weight.[33]

General findings: For all types of hydrolysis, some general findings are valid. The hydrolysis is easier and faster in a homogeneous medium, i.e., if PAN is in solution. PAN itself is practically insoluble in water. However, the addition of polar aprotic solvents (dimethylformamide, dimethyl sulfoxide, dimethylacetamide) to water enhances the solubility of PAN to a considerable extent. The presence of carboxyl and carboxamide groups in the PAN chain also accelerates hydrolysis. The polymers containing such groups are soluble in water, especially at elevated temperatures. In addition, these groups accelerate the hydrolysis of neighboring nitrile groups by their direct chemical participation in the reaction mechanism of hydrolysis.

3.0 EXPERIMENTAL DESIGN

The experiments performed in the first phase of this study were directed towards determining the chemical and radiation stability of PAN in the form of beads (B-PAN), similar to the beads of composite absorbers, and one selected composite absorber (AMP-PAN). Both B-PAN and AMP-PAN beads were prepared from the same polymer used in all the earlier studies. This polymer is the simplest to prepare, easiest to obtain, and cheapest of the PAN polymers.

The results of the review of the chemical properties of PAN showed that the type of polymer used is not optimal for stability in alkaline media. Nevertheless, because of the lack of data on its actual stability in the media tested and because of the other advantages given above, we decided to use this polymer for testing.

The methods selected for following the chemical and radiation stability included total bead volume measurement and swelling determination, complemented by microscopic examination and sieving analysis of the beads. For AMP-PAN, sorption capacity and distribution coefficient (K_D) values were determined, and the sorption kinetics of ^{137}Cs was measured.

3.1. Chemicals and Instrumentation

Both PAN beads (B-PAN) and composite absorber beads (AMP-PAN) were prepared following the general procedure given in Šebesta.[2] Beads of PAN were prepared using a modification of the general procedure that makes use of the coagulation of PAN when it is dissolved in an inert organic solvent. AMP-PAN composite absorber was prepared using the modification that makes use of the coagulation of PAN when it is dissolved in concentrated mineral acid. AMP-PAN composite absorber was prepared to contain 85.7% of ammonium molybdophosphate active component (dry weight). Dry powdered ammonium molybdophosphate was prepared in the laboratory following the published procedure.[35]

Nylon sieves "Uhelon" with exactly defined mesh size (Silk & Progress, s.r.o., Czech Republic) were used to wet-sieve out a fraction with grain size 0.7 – 1 mm for the experiments. The same sieves (mesh size 0.7, 0.85, 1.0, and 1.3 mm) were used for the sieving analyses. Sieving analyses of the original samples revealed that their grain size distribution within the interval 0.7 – 1 mm is nearly symmetric. For B-PAN, 49% of the beads had a grain size 0.7 – 0.85 mm and 51% had a grain size 0.85 – 1.0 mm. For AMP-PAN, 36% of the beads had a grain size 0.7 – 0.85 mm and 64% had a grain size 0.85 – 1.0 mm. Repeated sieving analyses of the sieved-out sample of B-PAN revealed that 1.2% and 0.4% of the beads passed the 0.7-mm sieve during the first or second repetition of the sieving, respectively. No beads were retained in the 1.0-mm sieve during any of the repeated sievings.

Aqueous 1M HNO_3 + 1M $NaNO_3$, 1M NaOH + 1M $NaNO_3$, and 1M NaOH solutions prepared from p.a. grade commercial preparations were chosen as simulants of DOE acidic and alkaline wastes. In addition, radiation stability was determined in distilled water. The ^{137}Cs tracer was a carrier-free solution of CsCl in 0.1M HCl (40 MBq ^{137}Cs in 0.63 mL, RCs-34, Poland). All other chemicals were p.a. commercial preparations.

Glass columns with volumes of ~150 mL (25-mm-diameter) equipped with a glass frit were used for the conditioning of the beads. A smaller glass column (volume ~100 mL; 20-mm-diameter) equipped with a glass wool plug at the bottom was used for bead washing and/or reconditioning. The flow rate was controlled by means of a peristaltic miniflow pump PCD 22 (Kouřil, Kyjov, Czech Republic). A water bath shaker (ELPAN 357, Poland), was used for gently shaking the samples during the contact period (speed 150 rpm, amplitude 8). The same shaker was used for the K_D determination (speed 130 rpm, amplitude 8).

For the column experiments, polypropylene Poly-Prep columns (BIO-RAD, USA.) equipped with a polyethylene frit with pore diameter 35 µm and 2 mL of bed volume of the absorbers were used. A four-blade propeller glass stirrer with LM III electrical mixer (Dioptra Turnov, Czech Republic) operated at a speed of 8 (maximum); a speed of 4 was used for sorption kinetics determination.

The γ-activity of the liquid samples was measured using an NV 3102 single-channel analyzer connected to a scintillation counter with a well-type NaI(Tl) detector (all Tesla, Czech Republic). In addition, standard laboratory equipment was used (pH-meters, mixers, centrifuge, ovens and/or drying ovens, etc.).

3.2. Evaluation of Chemical and Radiation Stability

3.2.1. Chemical Stability

Aqueous 1M HNO_3 + 1M $NaNO_3$, 1M NaOH + 1M $NaNO_3$, and 1M NaOH solutions were used as simulants of DOE acidic and alkaline wastes. The chemical stabilities of B-PAN and AMP-PAN beads were tested for a period up to one month of contact of the beads with the simulant solution.

Five samples of each of the conditioned beads (per 25 or 40 mL for B-PAN and AMP-PAN, respectively) were transferred into 100 mL polyethylene (PE) bottles. The total volume of the beads/solution mixture was adjusted to 50 mL or 60 mL for B-PAN or AMP-PAN beads, respectively, by adding the simulant solution tested. The rest of the conditioned sample was reconditioned back into distilled water (for B-PAN) or 10^{-3}M HNO_3 (for AMP-PAN) and used as a blank. The samples were continuously gently shaken at ambient temperature (21±2°C). All the samples were thoroughly mixed once a day.

After the required period of time, the total bead volume of the sample was measured and the sample was reconditioned back into distilled water or 10^{-3}M HNO_3 for swelling determination and eventual sieving analysis. All samples were subjected to visual/microscopic examination at the end of the testing period.

3.2.2. Radiation Stability

The same simulant solutions specified above were used in radiation stability testing. The radiation stability of B-PAN was also determined in distilled water; it was not determined in the acidic simulant where the results were expected to be similar to those found for AMP-PAN. Radiation stability testing of the beads was conducted in a radiation dose range 10^3 to 10^6 Gy.

Four samples of each of the conditioned beads (per 25 or 40 mL for B-PAN and AMP-PAN, respectively) were transferred into glass test tubes. Total volume of the beads/solution mixture was adjusted to 60 mL by adding the simulant solution tested. The test tubes were sealed by punctured glass stoppers to prevent pressure buildup of radiolytic gases during irradiation.[36]

The remainder of the conditioned sample was reconditioned back into distilled water (B-PAN) or into 10^{-3}M HNO_3 (AMP-PAN) and used as a blank.

The irradiations were performed in a ^{60}Co γ-radiation source PERUN (ARTIM, s.r.o., Czech Republic) at a dose rate of 2 kGy.hour^{-1}. The irradiation time extended from 30 minutes up to 22 days. The exact radiation dose was calculated from the known dose rate and actual irradiation time. The total volume of the samples irradiated up to 10^6 Gy had to be re-adjusted back to 60 mL with distilled water in the course of the irradiation (22 days) because of water evaporation and/or water radiolysis. At the end of the irradiation, the total bead volume of the sample was measured and the sample was reconditioned back into distilled water or 10^{-3}M HNO_3 (B-PAN or AMP-PAN, respectively) for swelling determination analysis. All the samples were subject to visual/microscopic examination at the end of the testing period.

3.2.3. Experimental Methods Used

Conditioning and reconditioning of the samples: The beads used for the testing were first conditioned by washing them with 10 bed volumes (BV) of the respective solution at a flow rate of ~ 5 BV.hour^{-1}. The conditioning was performed in two columns (75 mL of beads each). After contacting the samples with the simulants or exposing them to radiation, the samples were reconditioned back into distilled water (B-PAN) or 10^{-3}M HNO_3 (AMP-PAN). The initial flow-rate of 12 mL.min^{-1} was decreased after 30 minutes to 2 mL.min^{-1}; the samples were then flushed for an additional 1.5 hours at this flow rate.

Total bead volume measurement was performed in pre-calibrated 50 mL measuring cylinders. The beads were allowed to settle for 60 minutes under occasional tapping. Total bead volume was measured before the start of the experiment (after conditioning the samples), at the end of the experiment (in the simulant solution tested), and after reconditioning of the samples back into distilled water. Relative total bead volumes V_r and V_r^* were calculated by expressing the volumes measured at the end of the experiment and after reconditioning the samples, respectively, relative to the total bead volume before the start of the experiment.

Sieving analysis: Only those samples where significant changes in total bead volume were observed were submitted to sieving analysis. The reconditioned samples were wet-sieved using nylon sieves into groups with grain sizes < 0.7 mm, 0.7 – 1.0 mm, 1.0 – 1.3 mm, and > 1.3 mm. The volume of all the grain size fractions was measured using the procedure described above for total bead volume measurement.

Visual and microscopic examination: Changes in color and macroscopic mechanical properties of the beads and/or the supernatant solution were observed in the course of the tests and photographically documented (Practica BX20 camera, Germany) at the end of the experiments after reconditioning the samples back into distilled water. Microscopic changes of samples reconditioned back into distilled water were observed and photographically documented using a Type 2510 Microscope with MNF Photomicrographic Attachment (all PZO, Warszawa, Poland) and an Exakta VX 500 camera (Germany). Overall magnification was naturally dependent on the final photograph dimensions; for the format used for the presentation in this report (~12 × 8 cm), the magnification factor was ~40×.

Swelling measurements were performed in distilled water for B-PAN beads or in 10^{-3}M HNO_3 for AMP-PAN (to avoid decomposition of molybdophosphate complex ions). The beads were dewatered by centrifugation for 15 minutes at 3000 rpm (G = 6409 m.sec^{-2}) in a special glass tube equipped with a glass frit. The excess water was collected in absorbent cotton at the bottom of the tube. About 1.5 g of dewatered beads were then dried for 4 hours at 70^{0}C. Optimum revolution speed, time of centrifugation, temperature, and time of drying were determined in preliminary trial experiments. Swelling (*S*, contents of water, per cent) was calculated from the measured loss of weight following the formula

$$S = \frac{m_s - m_d}{m_s} \times 100 \qquad [\%]$$

where m_s is the weight of the aliquot of the swollen beads and m_d is its weight after drying to constant weight.

3.3. Evaluation of Sorption Properties of AMP-PAN

A determination of the changes in sorption properties of AMP-PAN was used for evaluating its chemical and/or radiation stability. AMP-PAN composite absorber reconditioned and dewatered by centrifugation as described above was used for determining the distribution coefficient (K_D), sorption capacity *(q)*, and sorption kinetics of the absorber for ^{137}Cs. All parameters were determined for the tested solutions of sodium nitrate in nitric acid. A 10^{-6} M CsCl solution, labeled by ^{137}Cs, was used for the determination of K_D and the kinetics of sorption. A 0.025M CsCl solution, labeled by ^{137}Cs, was used to determine the sorption capacity.

Determination of distribution coefficients was performed by contacting ~1 g of the exactly weighed swollen absorber with 50 mL of the solution after 20 hours of gentle shaking in a 250 mL PE bottle. Any absorber particles eventually remaining in the 2 – 3 mL aliquots of the water phase were removed by centrifugation for 3 minutes at 3000 rpm. Aliquots of 1 mL (diluted by 2 mL of distilled water) of this solution were taken to determine the γ-activities and the feed. Two parallel determinations were performed. K_D values were calculated using the equation

$$K_D = \frac{A_0 - A}{A} \times \frac{V}{m} \qquad [mL.g^{-1}]$$

where A_0 and A are background-corrected count rates of aliquots of the feed and test solutions after 20 hours of contact with the absorber, respectively; V is the volume of the water phase; and m is the mass of the swollen absorber.

Sorption capacity of AMP-PAN was determined by passing 25 mL of the feed solution in the downward direction through a Poly-Prep column with ~ 1 g of the exactly weighed swollen composite absorber. The absorber was pre-conditioned by washing with 10 mL of 1M HNO_3 + 1M $NaNO_3$ at a flow rate of 1 mL.min^{-1}. The column was closed by an air-tight lid to keep the solution level above the absorber constant. A flow rate of 0.3 mL.min^{-1} (10 BV.hr^{-1}) was controlled by means of a peristaltic pump. The effluent and all the washes were collected, and their volume was adjusted to 50 mL. Sorption capacity (q) of the absorber (per gram of the swollen absorber) was calculated using measured activities of aliquots of feed and effluent following the equation

$$q = \frac{N_1 - N_2}{m} = \frac{cV_f\left(1 - \frac{A_eV_e}{A_fV_f}\right)}{m} \qquad [mmole.g^{-1}]$$

where m is the weight of the tested sample of the absorber [g]; N_1 and N_2 are numbers of mmoles of CsCl in the feed and effluent, respectively; c is the molar concentration of CsCl in the feed [mole.L^{-1}]; A_f and A_e are activities of 1 mL aliquots of the feed and the effluent, respectively; and V_f and V_e are volumes of the feed and effluent [mL], respectively.

Kinetics of sorption: Approximately 1 g of the swollen AMP-PAN composite absorber was weighed and transferred into a glass vial. Then 50 mL of 10^{-6}M CsCl solution in 1M HNO_3 + 1M $NaNO_3$ labeled with ^{137}Cs were added. The mixture was immediately stirred using a glass propeller. Aliquots of 200 µL removed after 1, 5, 10, 20, 40, and 60 minutes of contact did not change the total volume significantly. These samples were rapidly (within 30 seconds) centrifuged at 3000 rpm; 100 µL aliquots were used for the γ-activity counting. Sorption yields (Y) were calculated from the activities of the feed and the samples using the equation

$$Y = \frac{A_0 - A_t}{A_t} \times 100 \qquad [\%]$$

where A_0 and A_t are the background-corrected count rates of aliquots of the feed solution and solution contacted with the absorber for the period t, respectively.

Swelling corrected values of distribution coefficients or sorption capacities (K'_D, q') were calculated from the same equations given above for K_D and q calculation by expressing these quantities per gram of **dry** composite absorber instead of per gram of **swollen** absorber. The weight of the dry absorber (m_d) was calculated from the weight of the swollen absorber used for the experiment and its swelling, following the equation

$$m_d = \left(1 - \frac{S}{100}\right) \times m_s \qquad [g]$$

where m_s is the weight of the swollen absorber and S (%) is its swelling determined as described above.

4.0 RESULTS AND DISCUSSION

4.1. Chemical Stability

Both B-PAN and AMP-PAN beads were contacted with 1M HNO_3 + 1M $NaNO_3$ solution (a simulant of DOE acidic waste). In addition, B-PAN was contacted with 1M NaOH + 1M $NaNO_3$ (a simulant of DOE alkaline wastes of Hanford type) or a 1M NaOH solution, selected to estimate the influence of high concentrations of nitrates. Contact periods of 1 day, 3 days, 7 days, 14 days, and 30 or 22 days were examined. A sample of beads contacted with the simulants and reconditioned into distilled water is shown in Photo 1.

The results of swelling and the relative total bead volume determination of B-PAN beads and AMP-PAN composite absorber are summarized in Table 3. In addition to these parameters, the main sorption properties (K_D, sorption capacity, and the kinetics of cesium uptake) determined for the AMP-PAN composite absorber are also shown in Table 3.

Table 3. Chemical Stability of PAN Beads (B-PAN) and AMP-PAN Composite Absorber in Simulant Solutions

Time of contact [days]	B-PAN		B-PAN		B-PAN		AMP-PAN					
	1M HNO_3 + + 1M $NaNO_3$		1M NaOH		1M NaOH + + 1M $NaNO_3$		1M HNO_3 + 1M $NaNO_3$					
	S [%]	V_r	S [%]	V_r	S [%]	V_r	S [%]	V_r	K_D [mL.g^{-1}]	q [mmole. g^{-1}]	K'_D [mL.g^{-1}]	q' [mmole. g^{-1}]
0	89.6	1.00	89.7	1.00	89.5	1.00	59.0	1.00	14100	0.16	34400	0.39
1	88.7	1.00	89.8	0.97	90.0	0.97	58.6	1.02	14500	0.17	34900	0.41
3	88.7	0.99	89.1	0.96	88.5	0.96	56.5	1.02	14100	0.16	32500	0.38
7	89.0	0.99	89.2	1.01	91.0	1.04	57.4	1.00	14300	0.17	33500	0.41
14	88.6	1.00	95.8	1.47	~99	2.31	57.9	0.98	15000	0.17	35600	0.41
30	89.6	0.98	NM^a	2.36^a	NM^a	NM^a	56.6	0.98	15800	0.18	36400	0.41

S - *swelling-contents of water [%] (average of two parallel determinations)*
K_D, K'_D - *distribution coefficients of* ^{137}*Cs [mL per gram of swollen or dry absorber, respectively]*
q, q' - *practical capacity for cesium (see text) [mmole per gram of swollen or dry absorber, respectively]*
V_r - *relative total bead volume, precision ± 0.02*
NM - *not measurable because of decomposition of PAN*
a - *22 days of contact only*

4.1.1. Stability of B-PAN and AMP-PAN in Acidic Simulant Solution

Excellent stability of both B-PAN and AMP-PAN beads was demonstrated. On the macroscopic scale, no coloration changes of either B-PAN or AMP-PAN beads were observed, even after one month of contact with the simulant (see Photo 1, columns 1 and/or 4).

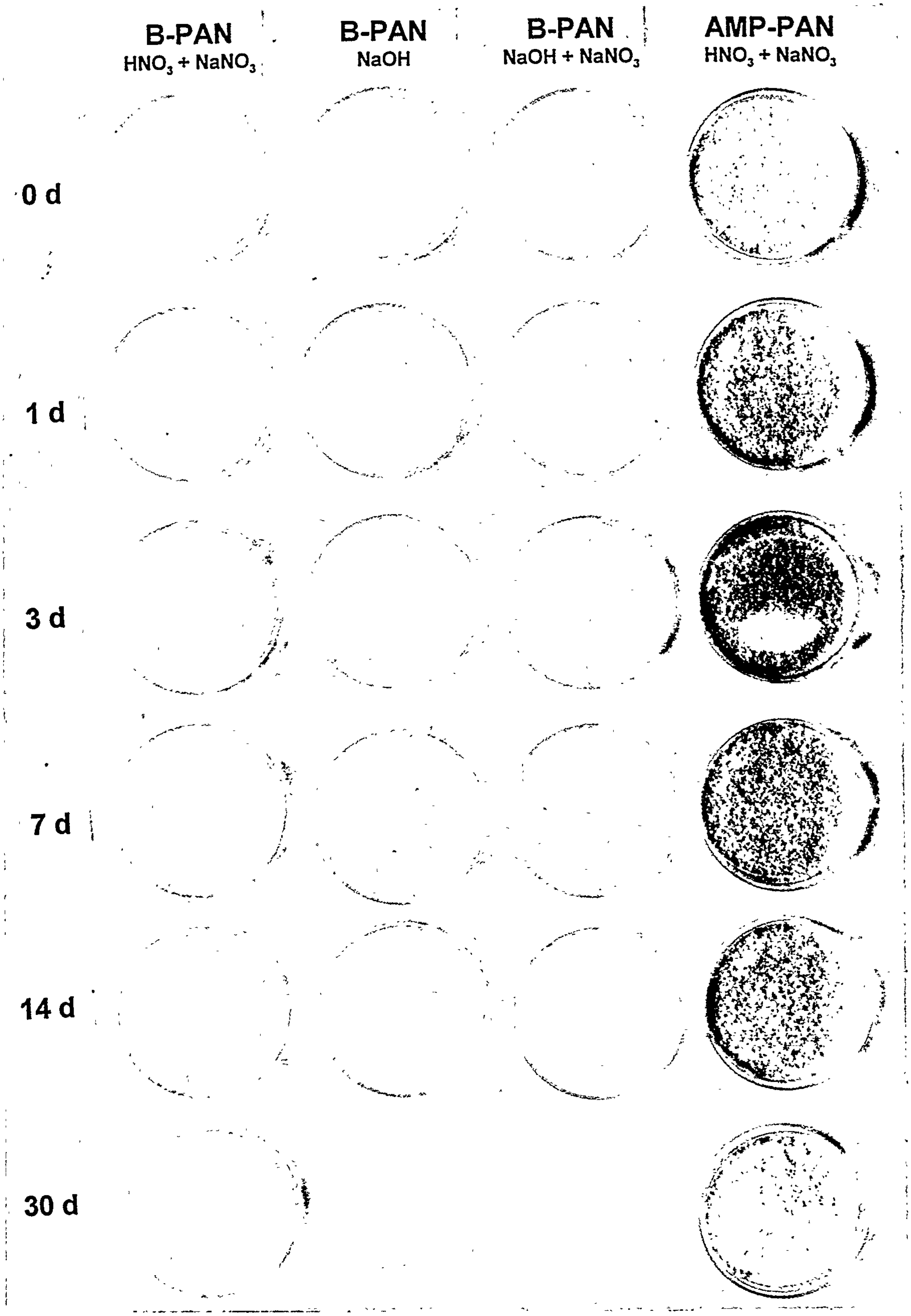


Photo 1. A view of B-PAN and AMP-PAN beads contacted for the given periods with single simulants of DOE acidic and alkaline wastes.

Microscopic examination revealed no cracking or any other mechanical damage for either B-PAN or AMP-PAN beads. In Photos 2 and 3, this microscopic stability is demonstrated in the microphotographs of the B-PAN blank (contact time of 0 days) and B-PAN contacted for 30 days with 1M HNO_3 + 1M $NaNO_3$ acidic waste simulant. A microphotograph of the AMP-PAN blank (contact time of 0 days) is shown in Section 4.2.2; the virtually identical microphotograph of AMP-PAN after 30 days of contact with acidic simulant solution is not shown.

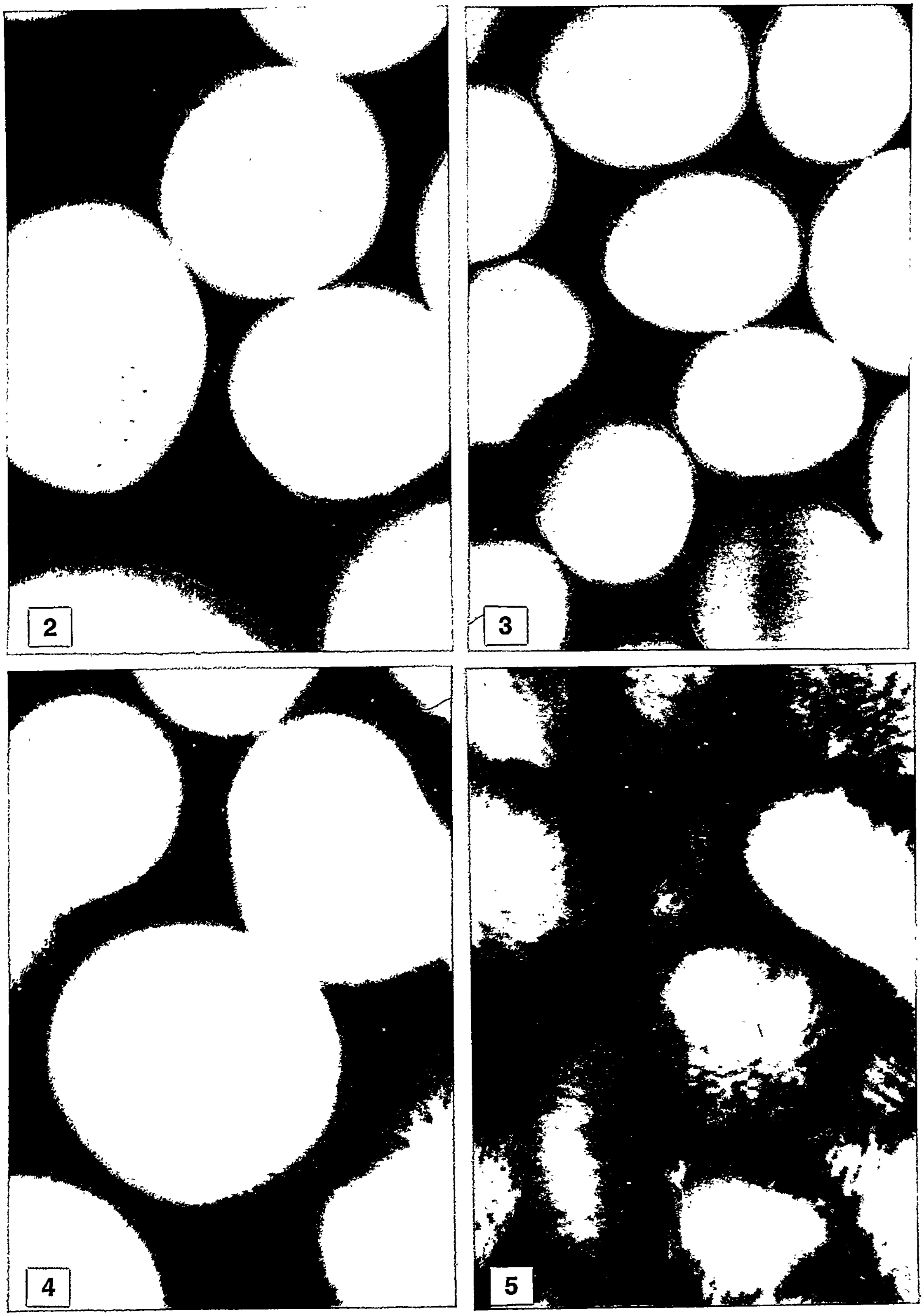
No significant changes of either **swelling or relative total bead volume** were observed during the contact time (see Table 3). The spread of the measured values reflects rather the precision of the experimental methods used (~2% for the relative total volume determination and 1 – 2% for swelling determination). The swelling values shown in Table 3 are average values of two parallel determinations. The difference between these parallel results was typically 0.1 – 0.2%. Reproducibility of the swelling determination was tested for some of the B-PAN samples and found to be much worse than the difference of the parallel analyses. The average results of repeated determinations differed by as much as 1%. Better accuracy of the results could not be achieved by increasing the number of parallel determinations because the total quantity of the tested beads was limited.

Closer examination of the AMP-PAN composite swelling-determination results shown in Table 3 indicates some possible decrease of swelling resulting from the contact time of the absorber with the simulant solution. This tendency cannot be definitely confirmed because of the somewhat limited accuracy of swelling determination mentioned above.

The difference in the swelling values of B-PAN and AMP-PAN beads reflects the different nature of the two types of the beads—pure polyacrylonitrile in B-PAN beads and a mixture of polyacrylonitrile (~15%) and AMP (~85%) in AMP-PAN composite absorber beads. Because of the absence of significant bead volume changes, neither B-PAN nor AMP-PAN beads were subjected to sieving analysis at the end of contact period.

The results discussed above not only validate the stability of PAN binder in the acidic waste simulant but also prove the absence of any possible negative influence (decomposition catalysis) of the ammonium molybdophosphate active component on the polyacrylonitrile binder. These results also demonstrate that the chemical stability of PAN (resistance to hydrolysis) is not influenced by the two procedures used to prepare the beads. The results are identical for the beads prepared from a solution of PAN in an organic solvent, B-PAN, and for the beads prepared from solution of PAN in a mineral acid, AMP-PAN (see Section 3.1.). This finding is important for the possibility of preparing AMP-PAN composite absorber by a simplified and cheaper procedure, bypassing the need to prepare dry powdered ammonium molybdophosphate.[2,3]

The results of **sorption properties testing** confirmed that the properties of PAN binder and the AMP active component do not deteriorate in contact with the acid simulant solution. To account for any potential systematic change of absorber swelling (see above), the swelling-corrected values (expressed per gram of dry weight of the absorber) of the distribution coefficients (K_D) and sorption capacities (q) were calculated in addition to the respective values expressed per weight of swollen absorber. No changes in the K_D values or sorption capacity (or swelling-corrected values) of the AMP-PAN composite absorber for cesium could be observed within the testing period. The spread of the values shown in Table 3 represents the precision of the experimental methods used rather than real changes of the quantities. Mean values found for



Photos 2–5. Microphotographs of B-PAN beads contacted with the simulants and reconditioned into H_2O; magnification ~ 40 *x* (*2* = blank; *3* = 1M HNO_3 + 1M $NaNO_3$, 30 days; *4* = 1M NaOH, 14 days; *5* = 1M NaOH + 1M $NaNO_3$, 14 days).

the swollen absorber are: $K_D \sim 1.5\times10^4$ mL.g^{-1} and $q \sim 0.17$ mmole.g^{-1}. Comparison of the K_D values and/or sorption capacity for cesium for the pure active component, AMP and AMP-PAN composite absorber, was not performed because earlier results[37] confirmed that the granulation procedure does not influence the sorption properties of PAN.

The results of determining the kinetics of uptake of ^{137}Cs by the AMP-PAN composite absorber are shown in Figure 1. Note that the two sorption-kinetics curves obtained for the blank and the sample contacted for 30 days with acidic simulant solution are virtually identical.

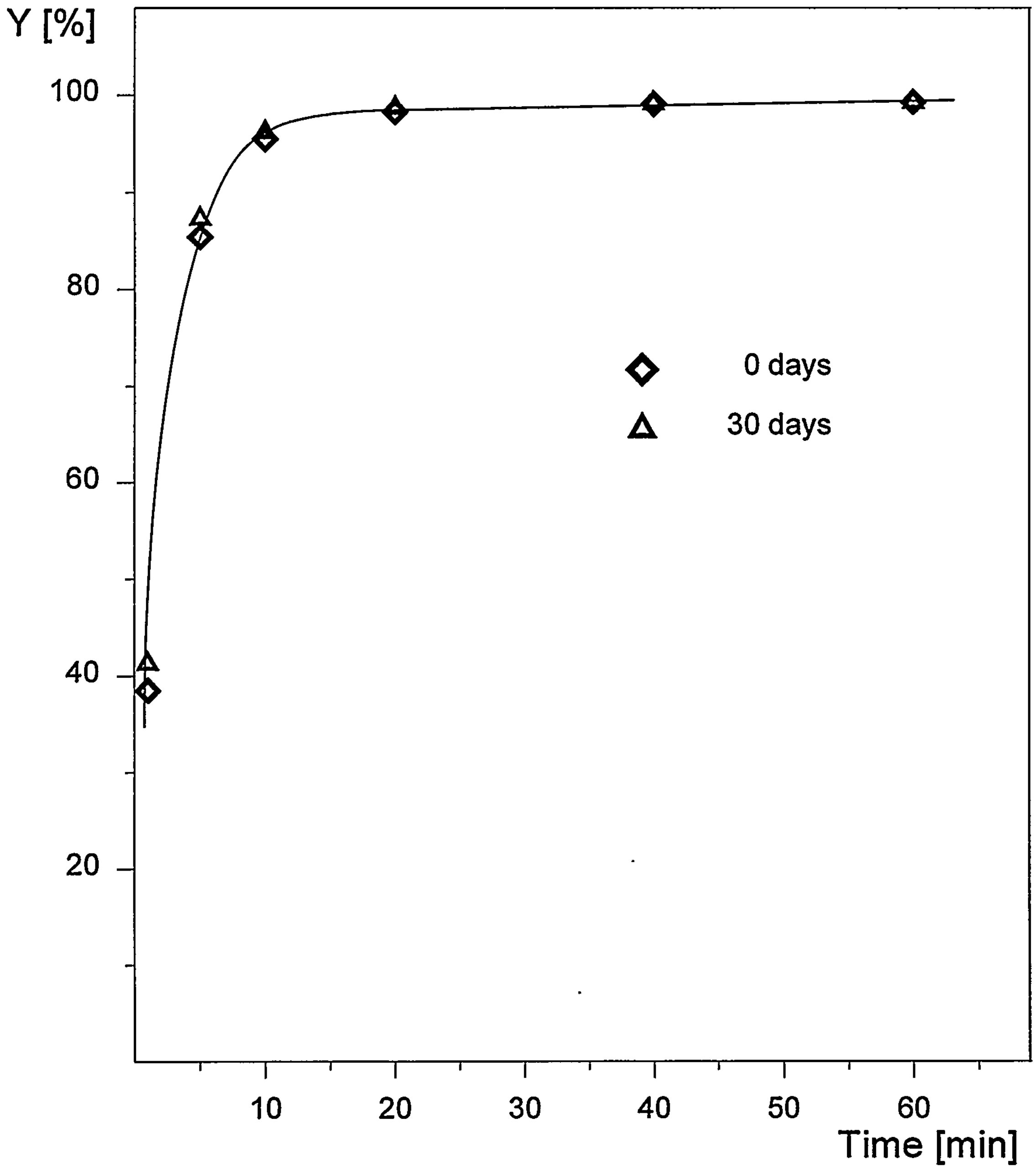


Figure 1. Dependence of uptake of ^{137}Cs by AMP-PAN composite absorber from 1M HNO_3 + 1M $NaNO_3$ solution over time.

Figure 1 also demonstrates a principal advantage of PAN-based absorbers: the rapid kinetics of ion uptake. The equilibrium sorption value is essentially reached in less than 10 minutes. Comparison of K_D values after 1 hour of contact between the absorber and the acidic simulant solution (7850 mL.g^{-1}) with the equilibrium K_D values (Table 3) indicates that the system has not reached equilibrium within this time. The cause is the slow diffusion of the cesium (which was initially sorbed rapidly onto the surface of the active-component particles) into these particles.

4.1.2. Stability of B-PAN in Alkaline Simulant Solutions

In these solutions, the stability of PAN beads was found to be limited. On the macroscopic scale, the first evidence of the ongoing changes was coloration of the B-PAN beads as early as during their conditioning. The initially white beads successively changed color through yellowish to yellow-brownish with increasing time of contact with the alkaline solutions. As discussed in Section 2.5, such changes of color are known to indicate transient formation of conjugated azapolyenes in the course of alkaline hydrolysis of polyacrylonitrile. Even a simple comparison of color changes of B-PAN beads in 1M NaOH and 1M NaOH + 1M $NaNO_3$ indicated much deeper changes occurring in the nitrate-containing solution. During the sample reconditioning back to distilled water, the color washed out of the beads; the resulting reconditioned B-PAN beads were again white, as seen in Photo 1.

The results of relative total bead volume measurement and swelling determination shown in Table 3 should be divided into two parts based on the time of contact of the beads with the solutions. For contact periods not exceeding 7 days, no significant changes of either relative total bead volume or swelling were observed for any of the simulant solutions. After 7 days of contact with 1M NaOH + 1M $NaNO_3$ solution, the first indications of possible hydrolysis appeared. Within this period not only was the relative total bead volume constant, but also the relative total volume of the reconditioned beads did not change. This is why no sieving analyses of these samples were performed. More significant changes of both relative total bead volume and swelling values appeared only between 7 and 14 days of contact with the solutions (see Table 3). From the results presented in Table 3, it also follows that the changes in the relative total bead volume are sensitively indicated by the changes of swelling values.

In 1M NaOH solution, a significant increase of total bead volume was found after 14 days of contact ($V_r = 1.47$). Additional pronounced increases in the total bead volume occurred during the reconditioning step ($V_r^* = 3.84$). Sieving analysis of the reconditioned samples revealed that no beads were smaller than 0.7 mm, 16% had a grain size 0.7 – 1.0 mm, 84% had a grain size 1.0 – 1.3 mm, and no beads were larger than 1.3 mm. The sieving analysis results are compared with the grain-size distribution of the original sample in Figure 2. The volume increase of the beads is probably ascribed to formation of carboxylate groups on the polymer skeleton during alkaline hydrolysis. Such carboxylate functional groups are typical for weakly acidic cation exchangers, which are characterized by larger changes of swelling at conversion from the Na^+- to the H^+-cycle, particularly in solutions with varying salinity[38]. For these exchangers, swelling typically increases with decreasing salinity of the solutions, as observed in experiments after the reconditioning. Experimental determination of the presence and concentration of the carboxylate groups in potential future testing analyses might confirm the proposed mechanism of hydrolysis. In this connection, determining the exchange capacity of the originally inert PAN, probably converted into a weakly acidic cation exchanger, would be of interest.

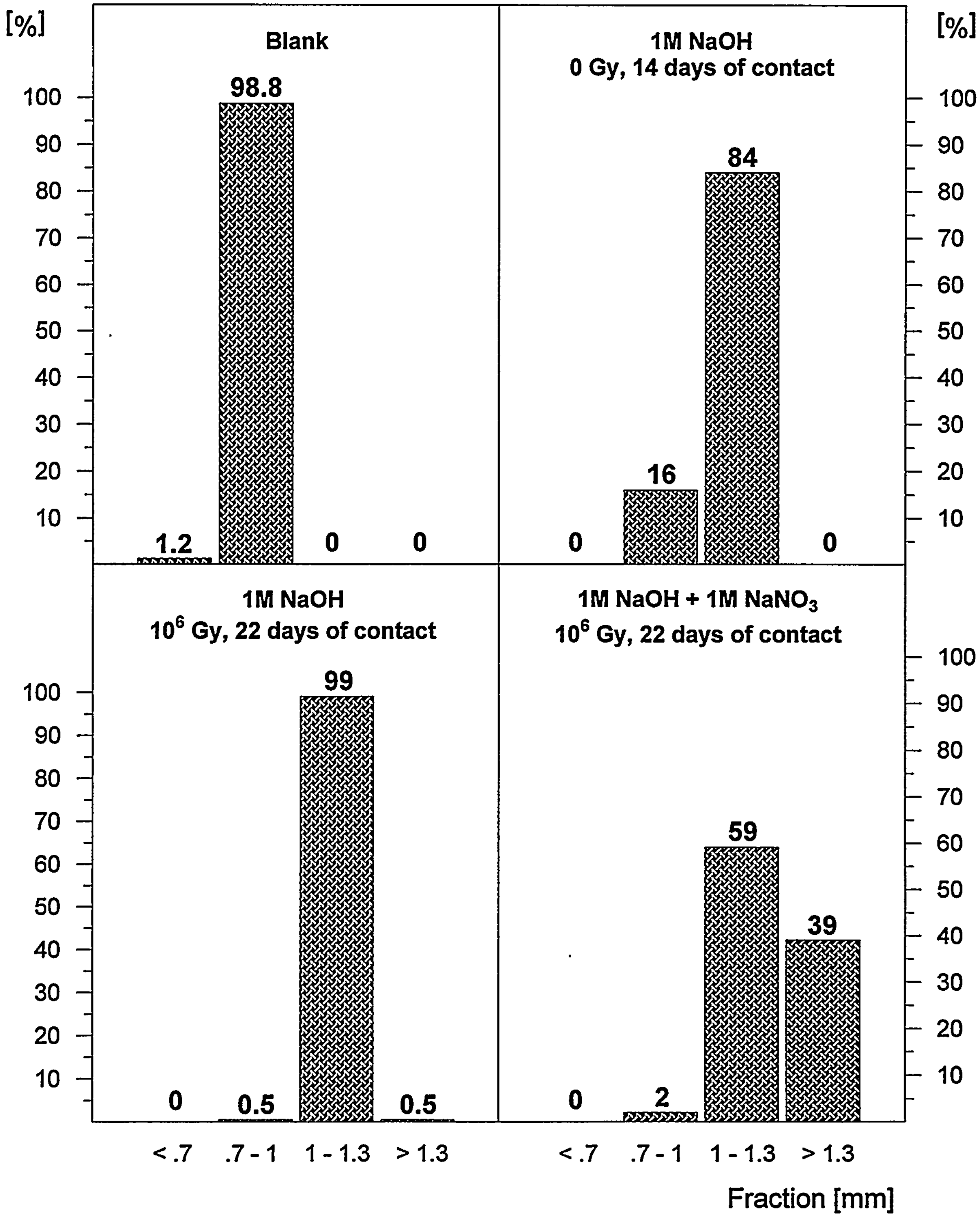


Figure 2. Bead size distribution of B-PAN after various periods of contact with simulant solutions and/or absorbed radiation doses (after reconditioning into distilled water).

The advanced degree of PAN hydrolysis may be also illustrated by comparing the microphotographs of the B-PAN blank (Photo 2) and hydrolyzed B-PAN (Photo 4). Nevertheless, note that for the sake of illustrating the chemical stability of PAN in alkaline solutions, microphotographs of the beads directly in the alkaline solutions (prior to reconditioning) should be compared. The reason for not doing so was that (on the basis of the results of the preliminary conditioning/reconditioning experiments) such large changes of bead volume and swelling were not expected.

Because of the evident significant hydrolysis of the B-PAN beads, the duration of the longest test was shortened to 22 days (from the originally anticipated 30 days). A large increase in the relative total bead volume was found in this test ($V_r = 2.36$). Single beads were cohesive but strongly gelled in 1M NaOH solution. The originally cohesive beads broke down completely during the reconditioning cycle and formed a white mass that slowly sedimented, forming a gelatin-like layer at the bottom of the beaker. No swelling determination could be performed for this sample.

In 1M NaOH + 1M $NaNO_3$ solution, increases of both the relative total bead volume and the swelling values after 14 days of contact between the beads and the solution were even more pronounced than for the 1M NaOH solution. Total bead volume more than doubled after this time of contact. The beads broke down completely during the reconditioning cycle. This fact is well demonstrated by the microphotographs in Photos 2 and 5. A high degree of hydrolysis is also reflected in the 99% swelling (see Table 3). After 22 days of contact, the beads disintegrated directly in the simulant solution, forming a gel. An opalescent solution of hydrolyzed PAN resulted from diluting this gel with water. None of the resulting quantities could be measured for this sample. The results corroborate that the hydrolysis of PAN in 1M NaOH solution is accelerated in the presence of sodium nitrate.

From the results achieved, it may be concluded that under the testing conditions PAN is stable enough for a period of at least 7 to 10 days. Even better stability may be expected in dynamic conditions where the degradation products of PAN will be continuously washed out. Such degradation hydrolysis products might further catalyze and accelerate PAN hydrolysis. The permanent shaking (though gentle) also presents conditions more harsh than may be expected in an absorber column application. For a more exact estimate of the maximum period of PAN-based absorber applicability, column experiments would have to be performed, preferably not with B-PAN beads but with one of the composite absorbers (e.g. NaTiO-PAN or TiO-PAN).

The stability period of PAN in strongly alkaline simulant solutions, though limited, may nevertheless be sufficient for most of the practical applications. This is because of the high sorption rate achievable with PAN-based composite absorbers; packed beds of these absorber are usually operated at high flow rates of 50 - 100 BV:hour^{-1}. At such flow rates, some 10,000 to 20,000 BV of waste could be treated within the 7 - 10 days of absorber stability. The sorption capacity of most active components (inorganic ion-exchangers) would be exhausted significantly earlier.

4.1.3. Influence of Concentration of NaOH on B-PAN Stability

Because of the detected limited stability of B-PAN in alkaline solutions, the planned experiments were supplemented by more detailed experiments designed to evaluate the influence of sodium hydroxide concentrations on the hydrolysis of PAN. The stability of the B-PAN beads was tested at two different lower alkali concentrations in 1M $NaNO_3$ (0.01M NaOH + 1M $NaNO_3$ and 0.1M NaOH + 1M $NaNO_3$). The concentration of sodium nitrate was thus maintained at the level proved to promote the hydrolysis. The results obtained are shown in Table 4, together with the results obtained earlier for 1M NaOH + 1M $NaNO_3$ (see Table 3).

Table 4. Influence of Concentration of NaOH on Chemical Stability of B-PAN

Time of contact [days]	**B-PAN**		**B-PAN**		**B-PAN**	
	0.01M NaOH + + 1M $NaNO_3$		0.1M NaOH + + 1M $NaNO_3$		1M NaOH + + 1M $NaNO_3$	
	S [%]	V_r	S [%]	V_r	S [%]	V_r
0	89.2	1.00	89.1	1.00	89.5	1.00
1	–	–	–	–	90.0	0.97
3	–	–	–	–	88.5	0.96
7	88.5	1.00	89.5	0.99	91.0	1.04
14	89.2	1.00	89.4	0.96	~ 99	2.31
21	89.3	1.00	89.0	0.96	NM[a]	NM[a]
30	89.3	1.04	88.7	0.96	–	–

S - *swelling-contents of water [%] (average of two parallel determinations)*
V_r - *relative total bead volume, precision ± 0.02*
NM - *not measurable because of decomposition of PAN*
a - *22 days of contact*

No changes in any properties of PAN could be observed after 1 month of contact with any of the solutions tested. No changes of either the relative total bead volume of B-PAN in the solution used or their volume after reconditioning into distilled water were found (see Table 4). The swelling values also remained unchanged (in the frame of the experimental errors). Therefore the samples were not submitted to sieving analyses.

From the results obtained it can be concluded that the dependence of PAN stability on the concentration of NaOH displays probably a threshold, above which the acceleration of PAN hydrolysis with increasing concentrations of NaOH is very progressive. Therefore conducting a more detailed study of PAN stability in the region of sodium hydroxide concentrations of 0.1 – 1 M might be of interest for practical applications of the type of polyacrylonitrile polymer used.

4.2. Radiation Stability

These experiments were directed towards establishing basic data on the radiation stability of swollen beads of binding polymer—PAN. Therefore distilled water was chosen as a reference medium. In a further series of experiments, B-PAN beads were irradiated in solutions simulating alkaline wastes (1M NaOH and 1M NaOH + 1M $NaNO_3$). In addition, the radiation stability of AMP-PAN composite absorber was studied in a simulant of acidic waste (1M HNO_3 + 1M $NaNO_3$ solution). These experiments doubled the number of experiments originally established for the frame of this project (i.e., irradiation of B-PAN in distilled water and AMP-PAN in acidic simulant only).[10]

The irradiation was carried out so as to deliver radiation doses ranging from 10^3 Gy to 10^6 Gy to single samples. Actual radiation doses were calculated from the total irradiation time and the known dose rate of 2 kGy.hour^{-1} (200 k rad.hour^{-1}) and amounted to 10^3 Gy, 10^4 Gy, $1.06.10^5$ Gy, and $0.98.10^6$ Gy. Irradiation times thus extended from 30 minutes up to 22 days. Therefore, for the higher radiation doses, not only did the influence of the radiation have to be considered, but also the influence of the chemical stability of the beads in the respective solutions had to be taken into account. A view of the samples of beads irradiated to the required radiation doses (after reconditioning into distilled water) is shown in Photo 6.

Evaluation of radiation stability was carried out using the same methods applied to the chemical stability study. The results of swelling and relative total bead volume determinations, of both B-PAN beads and AMP-PAN composite absorber, are summarized in Table 5, together with the results of the study of sorption properties of irradiated AMP-PAN composite absorber.

Table 5. Radiation Stability of PAN Beads (B-PAN) and AMP-PAN Composite Absorber in Various Media

Dose [Gy]	**B-PAN**		**B-PAN**		**B-PAN**		**AMP-PAN**					
	H_2O		1M NaOH		1M NaOH + + 1M $NaNO_3$		1M HNO_3 + 1M $NaNO_3$					
	S [%]	V_r	S [%]	V_r	S [%]	V_r	S [%]	V_r	K_D [mL.g^{-1}]	q [mmole. g^{-1}]	K'_D [mL.g^{-1}]	q' [mmole. g^{-1}]
0	89.8	1.00	89.9	1.00	89.7	1.00	59.0	1.00	14100	0.16	34400	0.39
10^3	89.6	1.00	89.5	0.98	89.8	0.97	59.2	1.05	13800	0.17	33800	0.41
10^4	89.4	1.01	89.4	0.96	89.3	0.97	58.9	1.03	14400	0.17	35000	0.41
10^5	89.0	1.00	88.3	0.96	88.5	0.97	57.4	1.01	14200	0.18	33400	0.41
10^6	88.5	1.00	95.3	2.28	97.8	3.54	56.5	0.99	14000	0.18	32300	0.41

S - *swelling-contents of water [%] (average of two parallel determinations)*
K_D, K'_D - *distribution coefficients of ^{137}Cs [mL per gram of swollen or dry absorber, respectively]*
q, q' - *practical capacity for cesium (see text) [mmole per gram of swollen or dry absorber, respectively]*
V_r - *relative total bead volume, precision ± 0.02*

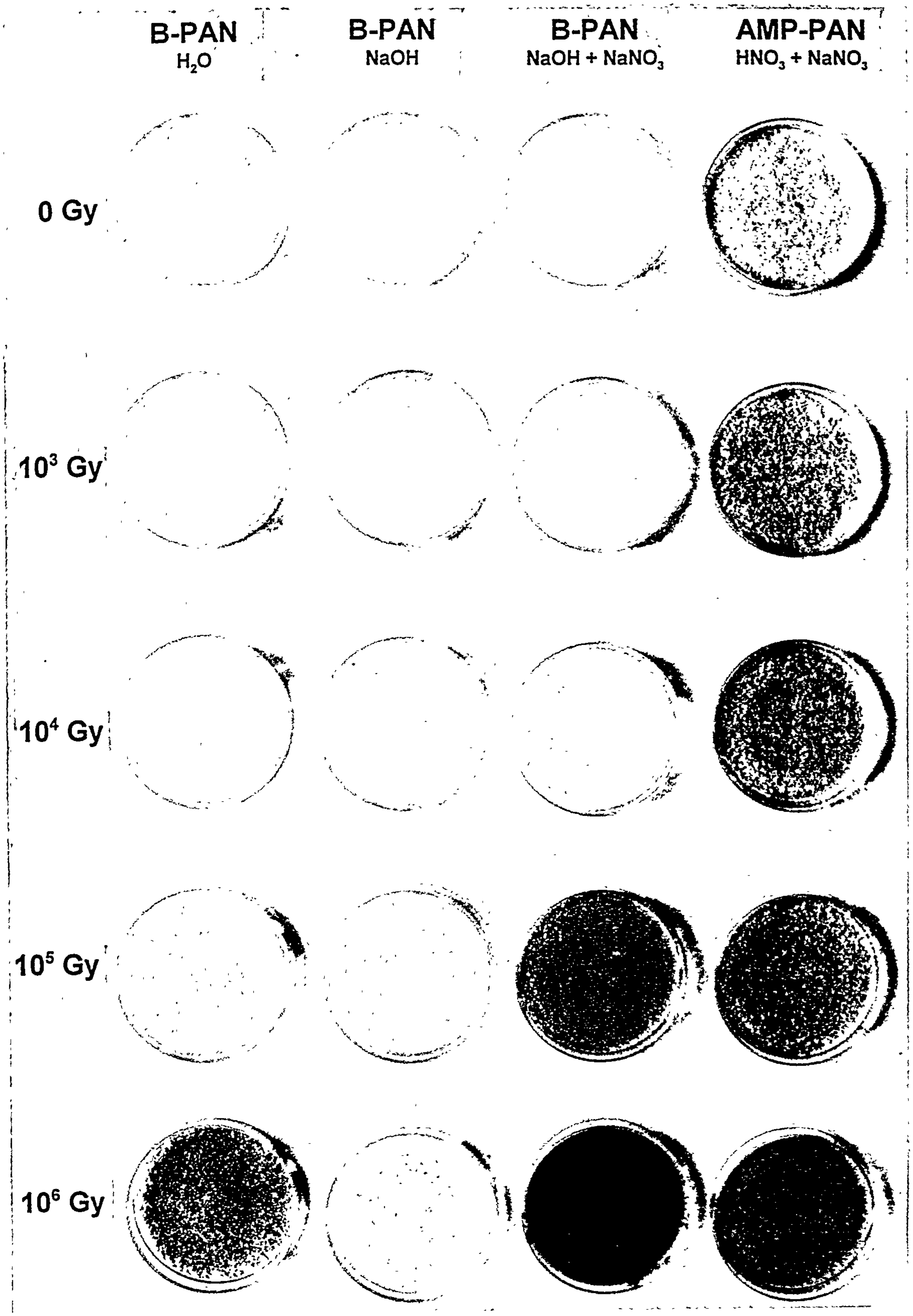


Photo 6. A view of B-PAN and AMP-PAN beads irradiated to the specified radiation doses in distilled water and single simulants of DOE acidic and alkaline wastes (after reconditioning into distilled water).

4.2.1. Stability of B-PAN in Distilled Water

On the macroscopic scale, only slight changes of color in the B-PAN beads could be observed. For the two highest radiation doses, the color of the beads changed to light-yellow and to a sand-like color, respectively. The supernate solution turned yellow for the absorbed radiation dose 10^6 Gy. Practically no color changes were observed during the reconditioning step. Microscopic examination revealed no cracking or any other mechanical damage to the beads. This microscopic stability is demonstrated in microphotographs of the B-PAN blank and a sample irradiated up to 10^6 Gy (Photos 2 and 9 respectively).

From the results presented in Table 5 it can be seen that B-PAN exhibits excellent radiation stability in distilled water up to a radiation dose of 10^6 Gy. No changes of either swelling or relative total bead volume were observed as a result of sample irradiation. Similar to the results of the chemical stability examination, the spread of the measured values reflects the precision of the experimental methods used. Because of the absence of significant bead volume changes, the samples were not subjected to sieving analysis after irradiation.

4.2.2. Stability of B-PAN in Alkaline Simulant Solutions

In alkaline simulant solutions, the radiation and chemical influences on the stability of the B-PAN beads are combined. On the macroscopic scale, radiation-dose-dependent coloration of the B-PAN beads and their supernate solutions could be observed. The initially colorless beads/solutions successively changed their color through yellowish to red-brownish with increasing absorbed doses. The coloration changes were much more pronounced (and appeared at lower absorbed doses) in the samples irradiated in the nitrate-containing simulant (see Photo 6, columns 2 and/or 3; and Photo 7). During the sample reconditioning back to distilled water, a significant part of the color was washed out of the B-PAN beads (see Photo 7). In this case it is remarkable that, after reconditioning, the samples irradiated in only NaOH underwent even weaker coloration changes than the samples irradiated in distilled water (see Photo 6, columns 1 and/or 2).

When comparing the results presented in Table 5 (irradiated samples) with the results in Table 3 (nonirradiated samples, 22 days of contact), a clear positive influence of γ-radiation on the stability of the binding polymer in alkaline media can be observed. Although the nonirradiated samples decomposed after 22 days, either during reconditioning back into distilled water (for 1M NaOH solution) or directly in the solution (in the presence of $NaNO_3$), the irradiated samples remained compact and exhibited finite swelling. This increase of stability is well demonstrated by comparing microphotographs of nonirradiated samples after 14 days of contact with 1M NaOH or 1M NaOH + 1M $NaNO_3$ solutions (Photos 4 and 5 respectively) with microphotographs of the corresponding samples irradiated up to 10^6 Gy within 22 days of contact (Photos 10 and 11). This effect may be unambiguously ascribed to PAN polymer cross-linking during irradiation and is thus an experimental confirmation of the theoretical assumption that polyacrylonitrile is a "rather cross-linking" polymer. A higher degree of cross-linking may manifest itself in higher mechanical strength of the polymer and/or its higher resistance to hydrolysis.

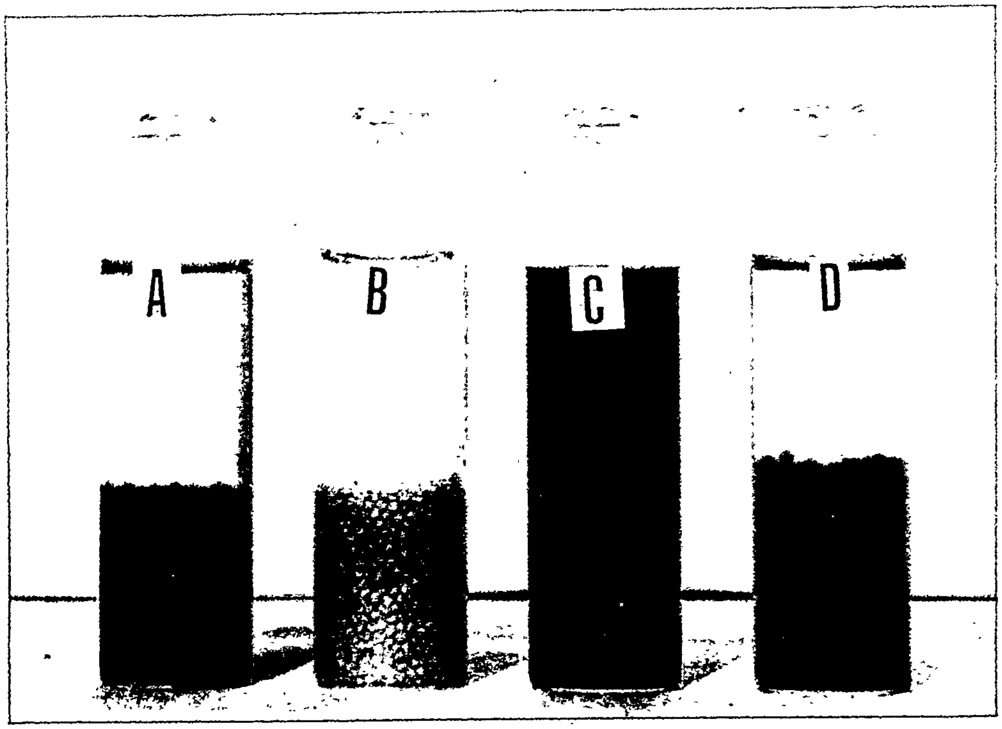


Photo 7. B-PAN beads irradiated up to 10^6 Gy, 22 days of contact (*A* = irradiated in 1M NaOH; ***B*** = "A" reconditioned in H_2O; ***C*** = irradiated in 1M NaOH + 1M $NaNO_3$; ***D*** = "C" reconditioned in H_2O).

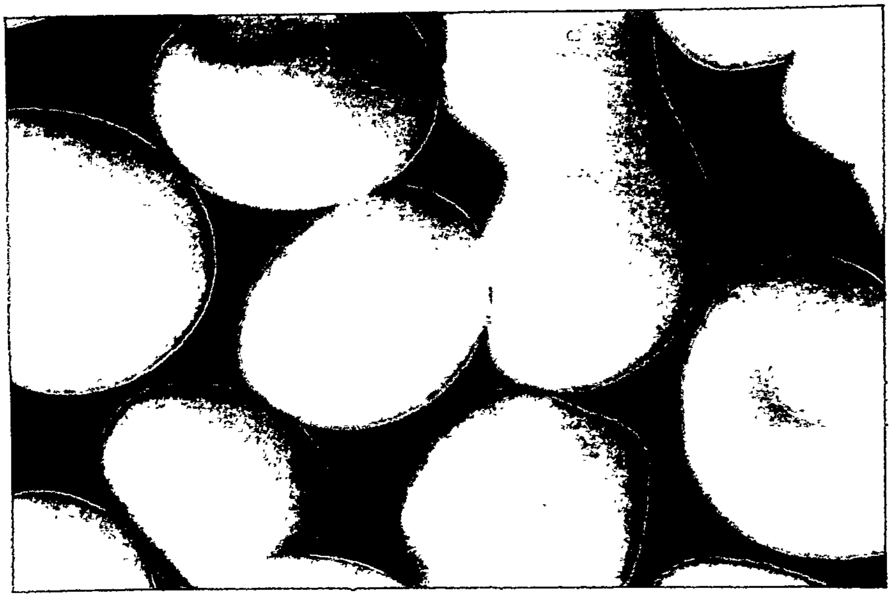
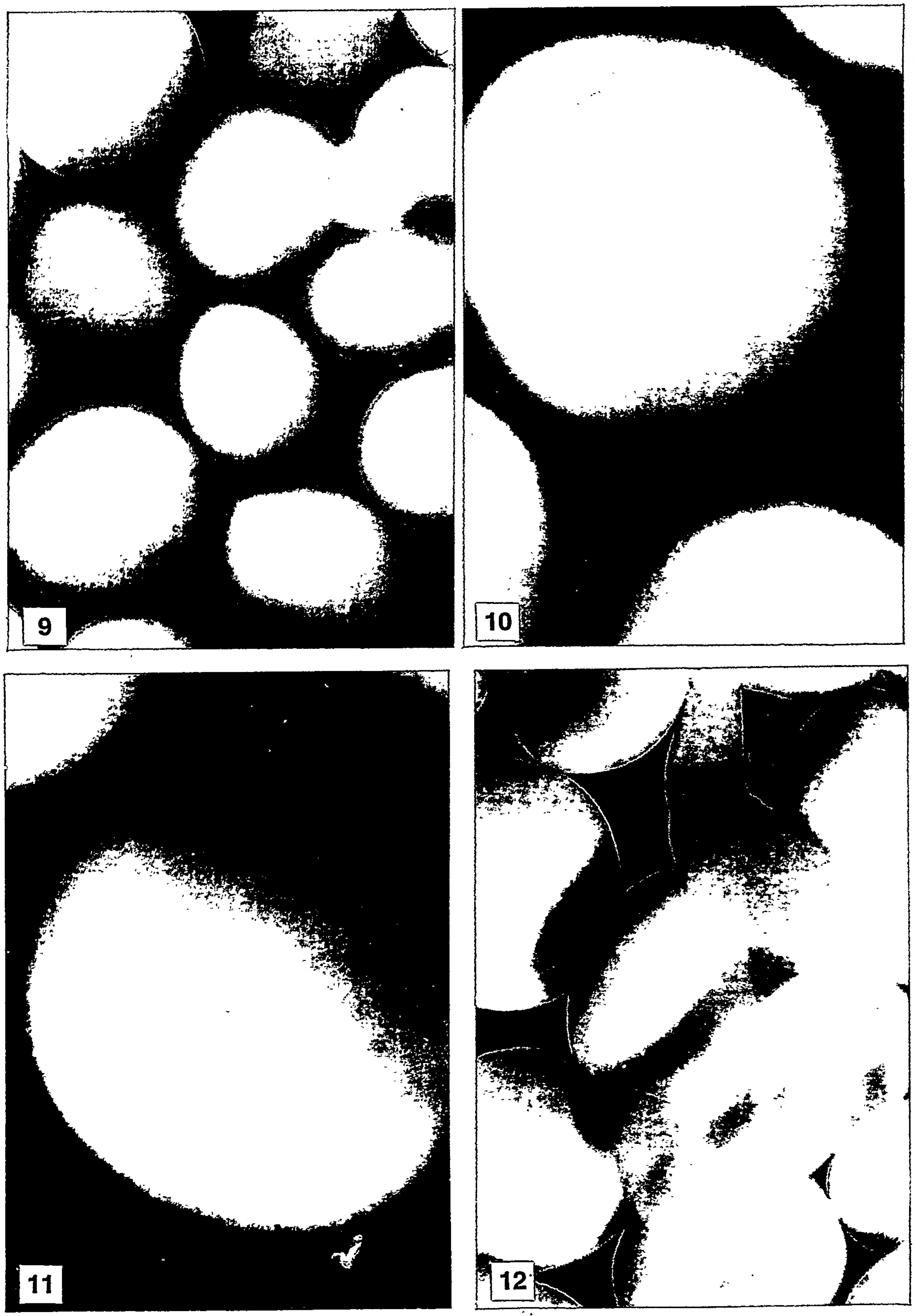


Photo 8. Microphotograph of the AMP-PAN composite absorber blank, magnification ~40× (0 days of contact with the simulant, 0 Gy).



Photos 9–12. Microphotographs of B-PAN and AMP-PAN beads irradiated up to 10^6 Gy; 22 days of contact, reconditioned into H_2O; magnification ~40× *(9* = B-PAN in H_2O; ***10*** = B-PAN in 1M NaOH; ***11*** = B-PAN in 1M NaOH + 1M $NaNO_3$; ***12*** = AMP-PAN in 1M HNO_3 + 1M $NaNO_3$).

The total bead volume of the samples was increasing to a similar extent, as observed during the chemical stability determination (relative volume of B-PAN after 22 days of contact with 1M NaOH was $V_r = 2.36$ or $V_r = 2.28$ for the nonirradiated and irradiated samples, respectively). The samples for which significant changes of bead volume were observed (i.e., the samples irradiated up to 10^6 Gy) were subjected to sieving analysis. Because the original samples were sieved in distilled water, the irradiated samples were reconditioned into distilled water also. During the reconditioning step, additional increases of volume occurred. Relative total bead volume of the reconditioned samples was $V_r^* = 4.09$ and $V_r^* = 4.42$ for the samples irradiated in 1M NaOH and 1M NaOH + 1M $NaNO_3$ solutions, respectively. Bead size distribution results and their comparison with the nonirradiated sample ("blank") are shown in Figure 2. From these results it can be seen that the increase of the relative total bead volume is not accompanied by any fractionation or breaking of the beads. The original grain size distribution pattern is simply shifted toward greater grain sizes. The magnitude of this shift is proportional to the relative total bead volume increase.

Similar to the results of the chemical stability determination, the results of relative total bead volume measurement, sample swelling, and sieving analyses clearly demonstrate the negative influence of the presence of $NaNO_3$ in NaOH on PAN stability. Nevertheless, note that for the irradiated samples this negative influence is much less than could be expected on the basis of the results of the study of chemical stability of B-PAN beads.

4.2.3. Stability of AMP-PAN in Acidic Simulant Solution

In the acidic simulant solution, excellent radiation stability of AMP-PAN beads was demonstrated. On the macroscopic scale, no changes of bead color were observed, even after irradiating them to 10^6 Gy within 22 days of contact with the simulant solution (see Photo 6, column 4). The supernate solution of the most irradiated sample (up to 10^6 Gy) was slightly green-yellow colored, probably a result of the formation of "molybdenum blue" by radiation-induced reduction of molybdophosphate complex anion. Microscopic examination revealed no cracking or any other mechanical damage of the beads. This microscopic stability is demonstrated in the microphotographs of the AMP-PAN blank and a sample irradiated to 10^6 Gy (Photos 8 and 12 respectively).

No changes of either swelling or relative total bead volume were observed as a result of sample irradiation (see Table 5). Similar to the results of the chemical stability examination, the spread of the measured values reflects the precision of the experimental methods used. Because of the absence of significant bead volume changes, the samples were not subjected to sieving analysis after irradiation. These results not only validate the radiation stability of PAN binder in acidic simulant solution to radiation dose 10^6 Gy, but also prove the absence of any negative influence of the ammonium molybdophosphate active component on the polyacrylonitrile binder under irradiation.

The results of **sorption properties testing** corroborated that the sorption properties of AMP-PAN were also not influenced by radiation. No negative changes in K_D values, sorption capacity (or their swelling corrected values), or the kinetics of uptake of ^{137}Cs by the AMP-PAN composite absorber could be observed within the tested range of absorbed radiation doses. Similar to the chemical stability determination, the spread of the values shown in Table 5 reflects the precision of the experimental methods used. Mean values found for the swollen absorber

($K_D \sim 1.4\times10^4$ mL.g^{-1} and $q \sim 0.17$ mmole.g^{-1}) are practically identical to the values found for samples from chemical stability testing.

While determining the kinetics of uptake of ^{137}Cs by the AMP-PAN composite absorber irradiated up to 10^6 Gy, it was found that the uptake of cesium by the irradiated absorber is more rapid than the uptake by the nonirradiated one (see Figure 3). This acceleration of kinetics can most probably be ascribed to fractionation of a part of the absorber beads. This fractionation was originally supposed to take place during vigorous stirring by the glass propeller (the electrical stirrer was operated at maximum revolution speed “8” to guarantee sufficiently good mixing). Nevertheless, it can also be seen from Figure 3 that decreasing the revolutions by one half (speed “4”), which should be gentle enough not to break the beads, resulted in only slightly slower cesium uptake. In the case of nonirradiated AMP-PAN, the rate of uptake of cesium at revolution speeds 4 and 8 was identical (compare Figures 1 and 3). The fractionation of the AMP-PAN beads thus probably occurred during the centrifugation, transfer, and/or weighing steps of the bead sample preparation process. This effect further demonstrates the influence of PAN polymer cross-linking during irradiation. A higher degree of cross-linking may manifest itself not only in higher mechanical strength but also in greater fractural fragility of the beads.

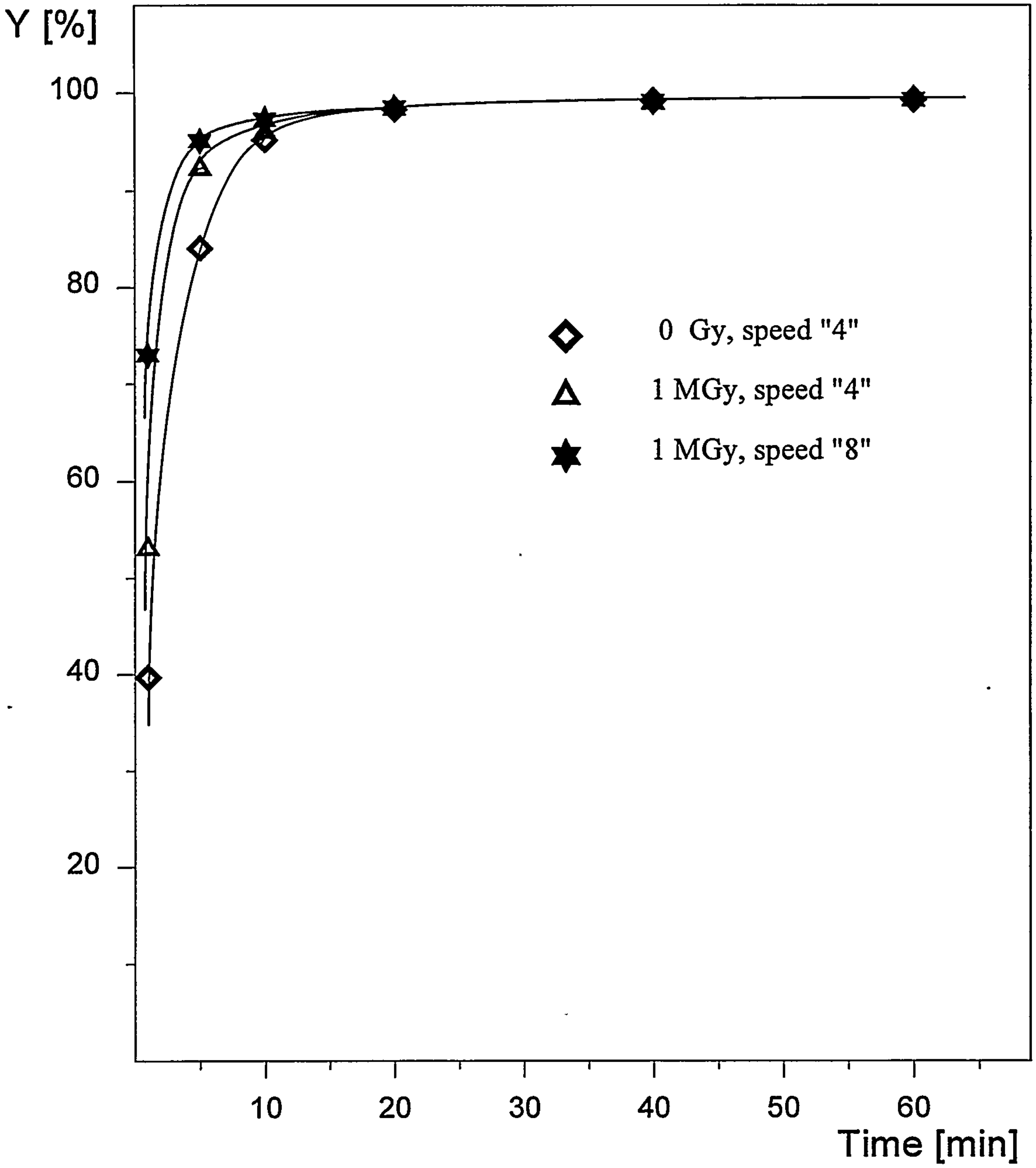


Figure 3. Dependence of uptake of ^{137}Cs by AMP-PAN composite absorber from 1M HNO_3 + 1M $NaNO_3$ solution on time and speed of stirring.

5.0 CONCLUSIONS

The results of the study of the chemical stability of PAN in the form of macroporous beads (B-PAN) similar to the beads of composite absorbers revealed their excellent chemical stability for a period of one month of contact with 1M HNO_3 + 1M $NaNO_3$, the solution used as a simulant of DOE acidic radioactive waste. The chemical stability of AMP-PAN composite absorber (ammonium molybdophosphate active component in PAN binder) was found to be as good as that of B-PAN beads. This result also proves the absence of any possible negative influence of the ammonium molybdophosphate active component on the polyacrylonitrile binder. No changes of sorption properties (K_D values, sorption capacity, or kinetics of uptake of cesium) of the AMP-PAN composite absorber were observed within the testing period.

Aqueous 1M NaOH + 1M $NaNO_3$ was used as a simulant of DOE alkaline radioactive waste. To enable evaluation of the influence of concentration of salts on the chemical stability of PAN binder in the alkaline media, the testing was performed in parallel in 1M NaOH solution. The chemical stability of B-PAN beads was found to be limited in these solutions. After 7 to 10 days of contact between the beads and the solutions, an increase of total bead volume, swelling of the beads, and grain size increases were observed in static tests. These changes were accompanied by coloration changes characteristic of PAN hydrolysis. The experimental results achieved proved that the hydrolysis of PAN in 1M NaOH is accelerated by the presence of sodium nitrate.

The study of the influence of concentrations of sodium hydroxide on the chemical stability of B-PAN revealed that in 0.1M NaOH + 1M $NaNO_3$, B-PAN is stable for the tested period of 1 month. The chemical stability of B-PAN beads is thus strongly influenced by sodium hydroxide concentrations in the range 0.1M - 1M NaOH. It can be concluded that the dependence of PAN stability on the concentration of NaOH displays probably a threshold, above which the acceleration of PAN hydrolysis with increasing concentrations of NaOH is very rapid.

Radiation stability of the PAN binder was found to be satisfactory to radiation doses 10^6 Gy for all the media tested (distilled water, 1M HNO_3 + 1M $NaNO_3$, 1M NaOH, and 1M NaOH + 1M $NaNO_3$). No changes of swelling or changes of total bead volume were observed for B-PAN or AMP-PAN irradiated in distilled water or 1M HNO_3 + 1M $NaNO_3$, respectively. Neither were any sorption properties of AMP-PAN influenced by the radiation. In alkaline simulant solutions, changes of B-PAN properties (total bead volume, swelling, color) were observed after irradiation to 10^6 Gy that took place within 22 days. All these changes may be ascribed to the limited chemical stability of B-PAN in these media. From the comparison of both the measured quantities and photo- or microphotographic documentation, the clear positive influence of γ-radiation on the stability of B-PAN in alkaline media can be seen. This effect may be unambiguously ascribed to PAN polymer cross-linking during irradiation, which manifests itself in higher resistance of the polymer to hydrolysis. This effect permits a longer useful period of PAN-based composite absorbers for treatment of alkaline high level wastes.

PAN is a versatile polymer capable of forming porous composite absorbers with small particles of a large number of primary absorbers. The composite absorbers are capable of withstanding harsh acidic and alkaline conditions and significant radiation doses.

In acidic solutions the stability of polyacrylonitrile binder is not limited by either chemical or radiation decomposition (within the range of conditions studied). PAN binder may thus be used for the preparation of composite absorbers for treatment of acid wastes from DOE facilities. The same conclusion is valid for alkaline solutions with pH up to 13.

In highly alkaline solutions (concentration of NaOH higher than 1 mole.L^{-1}) and in the presence of $NaNO_3$, the stability of the tested type of polyacrylonitrile polymer was sufficient for applications of composite absorber not extending over 10 days. Because of the high sorption rate achievable with these absorbers, sorption capacity of most active components will usually be exhausted earlier. The stability achieved is thus sufficient for most applications in the DOE complex.

The chemical stability of a binding polymer may be further improved by using another (more suitable) type of polymer from the broad family of polyacrylonitrile polymers to meet the requirement of higher stability in alkaline media (if necessary). Testing of possible candidate polymers is currently being initiated.

6.0 RECOMMENDATIONS

Recommendations for future studies to evaluate PAN as a binding polymer for absorbers used to treat liquid radioactive wastes are based on the above results and original experimental plans. These recommendations can be divided into two groups. The first summarizes some problems and/or areas of research, the study of which might significantly contribute to general knowledge of properties of polyacrylonitrile polymer and thus enable more exact evaluation and prediction of its behavior under conditions of potential full-scale applications. The second part of these recommendations summarizes possible modifications of the experimental plan for Phase II of this Project, following from the results obtained in this phase (Phase I) of the current project.

A general study of the chemical stability of the binding polymer should be directed, with studies in the following areas:

- Testing of the behavior and stability of B-PAN beads in alkaline media in dynamic experiments simulating real packed-bed application.
- Study of the chemical stability of B-PAN beads in alkaline media after preliminary irradiation of the beads in distilled water.
- The possibility of regenerating spent composite absorbers and the influence of such regeneration on their stability and repeated use should be studied.
- Verification of the proposed reason for the increase of swelling and/or mechanism of PAN hydrolysis—formation of carboxylate groups on the polymer skeleton in the course of alkaline hydrolysis.
- For the possibilities of technological application of selected composite absorbers to be considered, testing of chemical and radiation stability of these absorbers should be performed to exclude the negative influence of the respective active component(s) on the binding polymer stability in the liquid waste types considered.
- Selection and preparation of another polymer from the broad family of PAN polymers more suitable for application in highly alkaline media, and testing of its properties by the batch experimental methods developed under Phase I research.

Concerning the experimental program of Phase II of this project, the results obtained corroborated that AMP-PAN composite absorber might be selected for the demonstration of the performance of the binding polymer in acidic radioactive wastes. Testing this absorber with simulant solutions of stored acidic liquid radioactive wastes (e.g., at the Idaho Chemical Processing Plant) may be recommended. In packed-bed dynamic experiments, the efficiency of separation of cesium at various flow rates might be determined. In addition, the possibility of regenerating the absorber might be studied, and breakthrough curves of cesium would be determined.

Two possible modifications of the experiments originally planned to be performed in the alkaline simulant waste may be proposed on the basis of knowledge gained from Phase I. The first possibility is to follow the original plan and carry on similar experiments as proposed above for AMP-PAN absorber, using composite absorber containing either titanium dioxide (TiO-PAN) or zirconium phosphate (ZrP-PAN) as active components. From the results of the study of chemical stability of PAN beads (B-PAN) in alkaline media, it follows that the concentration of sodium hydroxide in the alkaline simulant solution selected for the study should not be higher than ~ 0.5 M.

Another possibility is to change the subject of this part of the Phase II study and perform some of the experiments that might significantly contribute to general knowledge of properties of polyacrylonitrile binding polymer, namely to its stability in alkaline media (as proposed above). Among the most worthwhile prospective topics for such a study are dynamic column experiments simulating real packed-bed applications of B-PAN beads that were tested in Phase I in batch experiments. Another possibility is to select and prepare another polyacrylonitrile polymer more suitable for application in highly alkaline media and test its properties by the batch experimental methods developed under Phase I research.

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APPENDIX

DEVELOPMENT OF PAN-BASED ABSORBERS FOR TREATING WASTE PROBLEMS AT U.S. DOE FACILITIES

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ABSTRACT

Polyacrylonitrile (PAN) can be used to bind together very small particles of absorbers into porous aggregates that can be used conveniently in packed columns. While binding the small particles together, the PAN allows substantial diffusion and even flow through the aggregates to give high effective mass transfer rates. Although PAN has been used or proposed for several applications, its capabilities for use with the U.S. DOE radioactive wastes have not been determined. This paper summaries studies at the Czech Technical University on the stability of PAN-based absorbers under the radiation, chemical, and physical conditions needed for DOE wastes and assessments of their potential performance with selected U.S. wastes.

INTRODUCTION

Highly specific absorbers and ion exchange materials are needed to treat wastes throughout the U.S. Department of Energy facilities. The needs range from removal of radionuclides from high-level wastes to treatment of groundwater, which can contain only traces of radioactivity. Specificity of the absorbers (or ion exchange material) for individual contaminants is important in minimizing the volume of concentrated waste eventually sent to disposal and to maximize the capacity and productivity of the sorption beds. This is important in high level wastes which are, in their liquid forms, highly concentrated salt and acid or base solutions. The radioactive contaminants are present at only trace concentrations, but are in the presence of high concentrations (several molar) of other components. If specific contaminants are to be removed at high concentrations, it is necessary for the absorber to be highly selective for the contaminant and reject the bulk components of the solution. This can be a highly demanding requirement because these solutions contain broad mixtures of components and usually have significant concentrations of the elements which have chemical properties closest to those of the contaminant.

Although the concentration of salts and other materials in groundwater are much lower, the concentrations of contaminants are also much lower. Unfortunately, the volume of these wastes can be relatively large in some cases, and it is highly desirable to control the cost by minimizing the quantities of harmless materials that are adsorbed with the contaminants.

There are also a number of wastes with intermediate concentrations such as low level wastes, process water, and mixed waste solutions which need selective adsorbents and extractants. The needs for improved and selective absorbers are similar to those for high level radioactive waste and groundwater. The concentration of contaminants may be between those of groundwater and high level waste, but the volume of these waste solutions may vary considerably.

Some of the most selective materials for removing ions from solution are inorganic materials that have intercrystalline layers or cavities with localized coordination points particularly appropriate for selected ions. These conditions can make such materials highly selective for such ions. A partial list of inorganic ion-exchangers that could be useful in radioactive waste treatment is given in Tab. 1. The stability of most inorganic materials in radiation fields can also be attractive feature of these materials for use in high level waste.

A major problem with such inorganic absorbers is the slow diffusion of all materials within the crystals of the absorbers. This problem is largely inherent to cases where the component is to be adsorbed within pores, layers, or cavities of the crystals. If the dimensions of these regions match the ion properties closely enough to result in high selectivity, it is likely that the openings for diffusion will be too small for rapid diffusion rates. To achieve acceptable adsorption rates, it is necessary to use very small particles to minimize the length of the diffusion

Table 1

EXAMPLES OF INORGANIC ION-EXCHANGERS THAT HAVE BEEN INCORPORATED IN PAN COMPOSITES

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
Ba[Ca]SO_4-PAN	Barium sulfate activated by calcium
CuS-PAN	Copper sulfide
Na-Y-PAN	Synthetic zeolite Na-Y
M315-PAN	Synthetic mordenite M315
CLIN-PAN	Natural clinoptilolite
HPM-PAN	Sr- and Ra-selective ternary
CAPM-PAN	ion-exchangers

paths. Because these absorber materials are also highly insoluble, it would sometimes be difficult to produce large crystals even if they were desired.

The small particles offer their own problems since beds of small particles offer high resistance to flow, and reasonable flow rates of liquid through packed beds of such particles would require unacceptable pressures. The standard approach to use small absorber particles is to incorporate the small particles into composites of larger particles. That is, "stick" the particles together into clusters with relatively large openings between the individual particles. The relatively large openings between the particles allow for higher diffusion rates within the larger particles, and the slow diffusion process within the crystalline particles can occur only over very short distances. Recent studies have shown that when the openings between the small particles are made sufficiently large, there can even be some flow through such composite particles within a packed bed, and this can increase the "effective" diffusion rate considerably (Watson, 1990; Carta et al., 1989; Watson, 1993).

One highly effective and relatively economical approach to creating porous composite particles of very small absorber particles involves binding the small particles into a porous polymer. Several polymers have been used for incorporating particles into such composites. A review of these processes was published recently by Šebesta and John (1995a). One particularly effective and interesting polymer (Šebesta, 1992) is Polyacrylonitrile (PAN). This material has been used to make composite particles of several small inorganic absorber particles (see Tab. 1), and several of these have found applications (Šebesta et al., 1993, 1994a, 1994b, 1994c).

PAN-based absorbers have been tested for prospective application for treatment of U.S. DOE liquid radioactive wastes at Los Alamos National Laboratory (Marsh et al., 1994a, 1994b, 1995, Svitra et al. 1994) and at Idaho Nuclear Engineering Laboratory since early 1994. Some applications of absorbers at the U.S. DOE facilities involve significant radiation and severe chemical conditions. The problems are most acute for high-level wastes which can involve intense radiation fields and highly alkaline or highly acidic conditions. This is why a project for "Evaluation of Polyacrylonitrile (PAN) as a Binding Polymer for Absorbers Used to Treat Liquid Radioactive Wastes" was initiated. The aim of this project has been to determine the stability of PAN and PAN-based absorbers under these harsh conditions. This paper summaries the first results of studies at the Czech Technical University in Prague performed under the radiation, chemical, and physical conditions needed for DOE wastes.

CHEMICAL AND RADIATION STABILITY OF PAN AND PAN BASED ABSORBERS

The experiments performed in the first phase of this study were directed towards determination of chemical and radiation stability of PAN in the form of beads similar to the beads of composite absorbers (B-PAN) and one selected composite absorber (ammonium phosphomolybdate - AMP-PAN, prospective for treatment of acidic wastes). Both B-PAN and AMP-PAN beads were prepared from the same polymer that has been used in all the earlier studies - the simplest to prepare, the easiest to receive and the cheapest of the variety of PAN polymers.

The methods selected for following the chemical and radiation stability included total beads volume measurement and swelling determination complemented by microscopic examination and sieving analysis of the beads. For AMP-PAN, changes in sorption capacity, distribution coefficient (K_D) values and kinetics of sorption of ^{137}Cs were determined.

Methods

1M HNO_3 + 1M $NaNO_3$, 1M NaOH + 1M $NaNO_3$, and 1M NaOH were chosen as simulants of DOE acidic and alkaline wastes. In addition, radiation stability was determined in distilled water. PAN beads (B-PAN) and ammonium phosphomolybdate composite absorber beads (AMP-PAN) were prepared following the general procedure of Šebesta (1992). Chemical stability of B-PAN and AMP-PAN beads was tested for a period up to one month of contact of the beads with the solution. Radiation stability of the beads was followed in a radiation dose range 10^3 to 10^6 Gy (10^5 to 10^8 Rad).

Total beads volume measurement was performed in a pre-calibrated 50 mL measuring cylinder. The beads were allowed to sediment for 60 minutes under occasional tapping.

Swelling measurements were performed in distilled water for B-PAN beads or in 10^{-3}M HNO_3 for AMP-PAN (to avoid decomposition of phosphomolybdate complex ion). The beads were dewatered by centrifugation for 15 minutes at 3000 rpm. ~ 1.5 g of dewatered beads were dried for 4 hours at 70^0C. Percentage swelling (contents of water) was calculated from the measured loss of weight.

Chemical Stability. The beads used for the testing were at first conditioned by washing them by 10 BV (bed volumes) of the respective solution at a flow rate of ~ 5 BV.hour^{-1}. 5 samples of the conditioned beads (per 25 or 40 mL for B-PAN and AMP-PAN, respectively) were transferred into 100 mL polyethylene (PE) bottles. 25 or 20 mL of the solution studied were added to the bottles with B-PAN or AMP-PAN beads, respectively. The rest of the conditioned sample was re-conditioned back into distilled water (B-PAN) or 10^{-3}M HNO_3 (AMP-PAN) and used as a blank. The samples were continuously gently shaken at ambient temperature. All the samples were thoroughly mixed once a day. After the required period of time total beads volume of the sample was measured and the sample was re-conditioned back into distilled water or 10^{-3}M HNO_3 (in the same way as given above for the blank) for swelling determination.

Radiation Stability. 25 mL of B-PAN or 40 mL of AMP-PAN conditioned in the same way as given for chemical stability were transferred into glass test tubes together with additional 35 or 20 mL, respectively, of the solution tested. The irradiation was performed in a 60Co γ-radiation source at a dose rate of 2 kGy.hour^{-1}. Total beads volume measurement, re-conditioning, and swelling determination was performed as described above.

Sorption Properties. ~ 1 g of AMP-PAN absorber dewatered by centrifugation as described above was used for the determination of K_D, sorption capacity, as well as sorption kinetics of the absorber for ^{137}Cs. All the parameters were determined for the solution tested - 1M HNO_3 + 1M $NaNO_3$. 10^{-6}M CsCl labeled by ^{137}Cs in this solution was used for K_D and sorption kinetics determination, 0.025M CsCl labeled by ^{137}Cs in this solution was used for sorption capacity determination.

K_D-determination was performed by contacting the absorber with 50 mL of the solution for 20 hours under gentle shaking. Any remaining absorber particles were removed from the water phase by centrifugation for 3 minutes at 3000 rpm. γ-Activities of aliquots of this solution and the feed were counted. K_D-values were calculated using standard formula.

Sorption capacity was determined by passing 25 mL of the solution through a Poly-Prep Chromatography column (Bio-Rad) with the absorber. Flow rate of 0.3 mL.min^{-1} was controlled by means of a peristaltic pump. The eluate and all the washes were collected, their volume was adjusted to 50 mL. Sorption capacity of the absorber (per gram of the swollen absorber) was calculated from the balance of ^{137}Cs activity calculated from the measured activities of aliquots of feed and eluate.

Kinetic of sorption was determined by vigorously stirring the absorber with 50 mL of the solution by a glass propeller. 200 µL aliquots were sampled periodically. The samples were rapidly (within 30 seconds) centrifuged at 3000 rpm, 100 µL aliquots were used for the γ-activity counting. Sorption yields (%) were calculated from the activities of the feed and the samples.

Swelling corrected values of distribution coefficients or sorption capacities (K_D', q') were calculated by expressing these quantities per gram of dry composite absorber instead of per gram of the swollen one.

Results and Discussion

Chemical Stability. The results of testing the chemical stability of PAN beads and AMP-PAN composite absorber are summarized in Tab. 2. These results demonstrate excellent stability of both B-PAN and AMP-PAN in the ***acidic simulant solution.*** No changes either of swelling or total beads volume were observed during one month of contact of the beads with the solution. Microscopic examination revealed no cracking or any other mechanical damage for either B-PAN or AMP-PAN beads. This finding not only validates the stability of PAN in these conditions, but also proves the absence of any possible negative influence (decomposition catalysis) of ammonium phosphomolybdate active component on the polyacrylonitrile binder.

The results of sorption properties testing corroborated that not only the properties of PAN binder, but also the AMP active component are not deteriorating in contact with acid simulant solution. No changes in K_D-values, sorption capacity (or their swelling corrected values), or kinetics of uptake of ^{137}Cs by the AMP-PAN composite absorber could be observed within the testing period. The two virtually identical sorption kinetics curves are shown in Fig. 1. This figure may also serve as a good demonstration of one of the main advantages of PAN-based absorbers - rapid kinetics of uptake of ions. The equilibrium sorption value is reached in less than 10 minutes!

In alkaline simulant solutions the stability of PAN beads was found to be limited. Negative influence of the presence of $NaNO_3$ in NaOH on PAN stability was found. The measured changes of swelling are much more dramatic than the changes of the total beads volume are. The reason of this fact is that the beads suffer mechanical damage during the re-conditioning cycle when transferred back to distilled water for swelling determination. This was well proved by microscopic examination of the beads. Total beads volume determination is thus better quantity for judging the stability of the beads.

Under the testing conditions, PAN was stable enough for a period of at least 7 to 10 days. Better stability may be expected in dynamic conditions where the degradation products of PAN will be continuously washed out. Such degradation hydrolysis products may further catalyze and accelerate the hydrolysis of PAN (Šebesta et al., 1995b).

Table 2

CHEMICAL STABILITY OF PAN BEADS (B-PAN) AND AMP-PAN COMPOSITE ABSORBER IN VARIOUS MEDIA

Time of contact [days]	B-PAN		B-PAN		B-PAN		AMP-PAN					
	1M HNO_3 + + 1M $NaNO_3$		1M NaOH		1M NaOH + + 1M $NaNO_3$		1M HNO_3 + 1M $NaNO_3$					
	S [%]	V_r	S [%]	V_r	S [%]	V_r	S [%]	V_r	K_D [$mL.g^{-1}$]	q [$mmole.g^{-1}$]	K'_D [$mL.g^{-1}$]	q' [$mmole.g^{-1}$]
0	89.6	1.00	89.7	1.00	89.5	1.00	59.0	1.00	14100	0.16	34400	0.39
1	88.7	1.00	89.8	0.97	90.0	0.97	58.6	1.02	14500	0.17	34900	0.41
3	88.7	0.99	89.1	0.96	88.5	0.96	56.5	1.02	14100	0.16	32500	0.38
7	89.0	0.99	89.2	1.01	91.0	1.04	57.4	1.00	14300	0.17	33500	0.41
14	88.6	1.00	95.8	1.47	~ 99	2.31	57.9	0.98	15000	0.17	35600	0.41
30	89.6	0.98	NM[a]	2.36[a]	NM[a]	NM[a]	56.6	0.98	15800	0.18	36400	0.41

Table 3

RADIATION STABILITY OF PAN BEADS (B-PAN) AND AMP-PAN COMPOSITE ABSORBER IN VARIOUS MEDIA

Dose [Gy]	B-PAN		B-PAN		B-PAN		AMP-PAN					
	H_2O		1M NaOH		1M NaOH + + 1M $NaNO_3$		1M HNO_3 + 1M $NaNO_3$					
	S [%]	V_r	S [%]	V_r	S [%]	V_r	S [%]	Vr	K_D [$mL.g^{-1}$]	q [$mmole.g^{-1}$]	K'_D [$mL.g^{-1}$]	q' [$mmole.g^{-1}$]
0	89.8	1.00	89.9	1.00	89.7	1.00	59.0	1.00	14100	0.16	34400	0.39
103	89.6	1.00	89.5	0.98	89.8	0.97	59.2	1.05	13800	0.17	33800	0.41
104	89.4	1.01	89.4	0.96	89.3	0.97	58.9	1.03	14400	0.17	35000	0.41
105	89.0	1.00	88.3	0.96	88.5	0.97	57.4	1.01	14200	0.18	33400	0.41
106	88.5	1.00	95.3	2.28	97.8	3.54	56.5	0.99	14000	0.18	32300	0.41

S - *swelling (contents of water) [%]*
K_D, K'_D - *distribution coefficients of* ^{137}Cs *[mL per gram of swollen or dry absorber, respectively]*
q, q' - *practical capacity for cesium (see text) [mmole per gram of swollen or dry absorber, respectively]*
V_r - *relative volume of the absorber (relatively to its initial volume), precision ± 0.02*
NM - *non-measurable because of decomposition of PAN*
a - *22 days of contact only*

Because of high sorption rate achievable with PAN-based composite absorbers packed beds of these absorber are usually operated at flow rates 50 - 100 $BV.hour^{-1}$. At such flow rate some 10,000 to 20,000 BV of waste could be treated within the 7 - 10 days of sufficient stability of the absorber. Sorption capacity of most active components (inorganic ion-exchangers) would be exhausted significantly earlier. Thus the stability of PAN binder in alkaline simulant solutions, even though limited, is sufficient for most of the practical problems.

In additional trial experiments PAN stability at lower alkalis concentrations was tested. Preliminary results indicate that the dependence of PAN stability on the concentration of NaOH displays a threshold. In 0.1M NaOH, no changes in PAN stability were observed after approximately 1 month of contact.

Radiation Stability. The results of testing the radiation stability of PAN beads and AMP-PAN composite absorber are summarized in Tab. 3. No influence of radiation on the stability of PAN was found up to the total absorbed dose of 10^6 Gy (10^8 Rad) for B-PAN irradiated in distilled water. Neither any changes of swelling nor changes of total beads volume were observed. Nor microscopic examination could reveal any changes or damage of the beads structure.

Radiation stability of AMP-PAN in acidic simulant solution was found to be as good as that of B-PAN in distilled water. No negative influence of either the acidic simulant solution or the presence of ammonium phosphomolybdate active component was observed. Sorption properties of AMP-PAN (K_D-value and/or sorption capacity for ^{137}Cs) were not influenced by radiation, either.

During determination of kinetics of uptake of ^{137}Cs by the irradiated absorber lower mechanical strength of the beads was found. Some of the absorber beads were broken during vigorous stirring by the glass propeller, which resulted in further acceleration of sorption kinetics (see Fig. 1). This

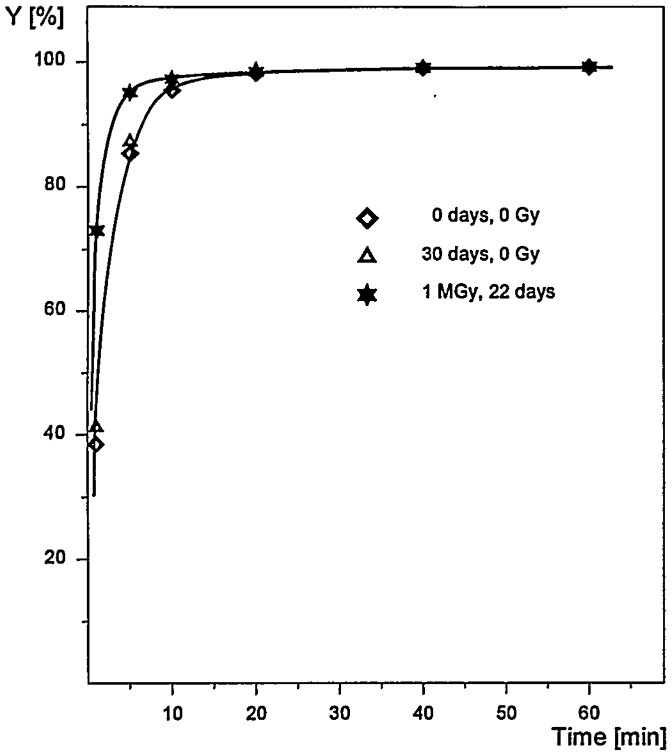

Fig. 1

DEPENDENCE OF KINETICS OF UPTAKE (Y) OF ^{137}Cs BY AMP-PAN COMPOSITE ABSORBER ON THE TIME OF CONTACT OF THE ABSORBER WITH 1M HNO_3 + + 1M $NaNO_3$ SOLUTION AND/OR RADIATION DOSE

effect may be unambiguously ascribed to PAN polymer cross-linking during irradiation. Higher degree of cross-linking may manifest itself in hardening and higher fragility of the polymer.

In alkaline simulant solutions two effects are combined. Higher radiation doses require relatively long irradiation time - in our experiments 22 days were needed for irradiating the beads up to 10^6 Gy. Therefore, in addition to the influence of radiation, influence of chemical stability in alkaline media has to be considered. When comparing the results presented in Tab. 3 (irradiated samples) with the results in Tab. 2 (unirradiated samples, 22 days of contact), clear positive influence of these combined effects on the stability of the binding polymer can be observed. While the unirradiated samples decomposed after 22 days either during re-cycling into distilled water (for 1M NaOH solution) or directly in the solution (in the presence of $NaNO_3$), the irradiated samples remained compact and exhibited finite swelling. This effect is another (positive) consequence of the cross-linking of the polymer discussed above.

CONCLUSIONS

PAN is a versatile polymer capable of forming porous composite absorbers with small particles of any of a large number of primary absorbers. The composite absorbers are capable of withstanding harsh acidic and alkaline conditions and significant radiation doses.

In acidic solutions the stability of polyacrylonitrile binder is not limited by either chemical or radiation decomposition (within the range of conditions studied). PAN binder may thus be used for preparation of composite absorbers for treatment of acid wastes from DOE facilities. The same conclusion is valid for alkaline solutions with pH up to 13.

In highly alkaline solutions (concentration of NaOH higher than 1 mole.L^{-1}) and in the presence of $NaNO_3$ the stability of the tested type of polyacrylonitrile polymer was sufficient for applications of composite absorber not extending over 10 days. Because of high sorption rate achievable with these absorbers, sorption capacity of practically any active component will be usually exhausted earlier. The stability achieved is thus sufficient for most applications in DOE complex.

The chemical stability of binding polymer may be further improved by using different type of polymer from the broad family of polyacrylonitrile polymers (Šebesta et al., 1995b) so as to meet the requirement of higher stability in alkaline media (if necessary). Testing of possible candidate polymers is currently being initiated.

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