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## INVESTIGATIONS ON REACTIVE POLYMERS USING AUTORADIOGRAPHY AND SCANNING ELECTRON MICROSCOPY

Significant improvements in fundamental knowledge of mass transport in diffusional studies in reactive polymers may be achieved by autoradiography and scanning electron microscopy. Review of these techniques with application to investigation on desulphation process of sea or brackish water is presented.

### 1. INTRODUCTION

Autoradiography technique based on the use of films sensitive to nuclear radiations may give direct information on the distribution of labelled species within solid materials. Although the technique has long been used in metallographic [2, 9], semiconductor [5], and biomedical studies [6, 13], there are relatively few examples of the application of autoradiography to reactive polymer science, particularly to ion-exchange and membrane technology [1, 10, 11].

By combining autoradiographic data on the distribution of species of interest inside a solid (an ion-exchange resin, for instance) with the analysis of the polymer matrix morphology, as given by scanning electron microscopy (SEM), extremely useful information on diffusion and reaction mechanisms can be obtained.

A combined use of autoradiography and SEM techniques has been recently introduced at the IRSA to investigate ion-exchange mechanism during desulphation treatment of sea (or brackish) water feeding distillation plants [4, 7, 8].

We believe that a detailed description and recommended operating conditions for the application of these techniques to study ion-exchange mechanisms presented in this note can be easily extended to other water and wastewater treatments by reactive polymers.

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## 2. AUTORADIOGRAPHIC METHODS

Autoradiography relies on the ability of some emulsion to detect radioactive emissions from radionuclides.

Under proper operating conditions  $\alpha$ ,  $\beta$  and  $\gamma$  emissions produce a well localized spot on the emulsion being in contact with the specimen to be autoradiographed in correspondence of the incident point of each radiation. It is thus possible to have a visible localization of the distribution of radioelements in a solid, after a given sample (e.g. an ion-exchange resin) has been loaded with a radioactive nuclide.

Sections of the active material are put in a close contact with a nuclear emulsion in a dark room, according to the following techniques:

direct contact: the emulsion supported by a plastic film is put directly on the sample to be analyzed,

stripping: a thin layer of nuclear emulsion mounted on a glass plate is cut and stripped from the plate to be applied on the specimen,

dipping: the sample to be autoradiographed placed on a glass slide is immersed into a liquid nuclear emulsion of the known viscosity to have a controlled thickness of emulsion covering the specimen.

The thickness of the emulsion influences primarily the resolution and the efficiency of the autoradiography. Better resolution and poorer efficiency are usually obtained with "dipping", if compared with "direct contact" or "stripping" techniques. The latter, indeed, are used preferably in quantitative diffusional studies where the principal goal is the elemental distribution.

Particular attention must be given to preparation of sample to be autoradiographed. Sufficiently thin (1–100  $\mu\text{m}$ ) slices are obtained with microtomes. Material to be microtomed is preferentially embedded into plastics to avoid its breakdown.

After processing with standard photographic treatment, the observation of autoradiographic tracks is better performed by a light microscope, where the blackening intensity (optical density of discrete regions of the autoradiogram) may be measured by a microdensitometer.

Accurate autoradiogram observation may be obtained by scanning electron microscopy, where radioisotopic distribution at molecular level can be detected.

For a general description of fundamentals and basic application of autoradiography, the interested reader is referred to a comprehensive book by ROGERS [14].

## 3. SCANNING ELECTRON MICROSCOPY

Scanning electron microscopy, developed as early as in 1965 [15], essentially consists of an electron beam (primary electrons) scanning the surface of a solid sample and producing the emission of secondary electrons and electromagnetic radiation (X-rays). By detecting these secondary electrons it is possible to obtain an amplified image of the sample surface on an high persistence cathode ray tube (emissive mode of operation).

Resolution, magnification, and depth of focus with SEM are some orders of magnitude larger than with light microscopy. Contrast and resolution of the image are directly correlated to the yield of secondary electrons detected, which in turn depend on a correct choice of primary beam energy (to be compatible with specimen burning) and on a good orientation of the incident beam toward the specimen.

With ion-exchange resins and similar fairly non-conductive polymers, burning of the sample is likely to occur. To avoid this, low energy beam of primary electrons must be coupled to a good covering of sample with a thin layer ( $\sim 200 \text{ \AA}$ ) of metal (Au, Pd) or of graphite. Such a covering operation, performed usually by vacuum evaporation, is very delicate and may introduce artefacts and irreversible modification of ion-exchange sample [12].

#### 4. APPLICATIONS

The desulphation process, developed at IRSA since 1974 [3, 16], is a pretreatment of sea or brackish water by ion-exchange resins to avoid precipitation of  $\text{CaSO}_4$  in evaporation, reverse osmosis and other concentration processes. To this aim the feed water is pretreated by an ion-exchange resin in chloride form to substitute its sulphates according to the ion-exchange reaction:



The exhausted resin is regenerated by the concentrated stream disposed from the evaporation plant. The plant can accordingly be operated at concentration factor and maximum temperature up to 4 and  $150^\circ\text{C}$ , respectively, quite above the values of 1.8 and  $112^\circ\text{C}$  usually adopted for distillation of non-desulphated sea water.

For a better comprehension of diffusional mechanism during  $\text{Cl}^-/\text{SO}_4^{=2}$  ion-exchange process, a combined use of autoradiography and SEM has been recently coupled with previous investigation based on standard radioanalytical and potentiometric techniques [4, 7, 8].

In planning autoradiographic experiments on ion-exchange resins the following parameters must be optimized:

- embedding material,
- sample—emulsion contact technique,
- type of emulsion,
- emulsion thickness (dipping or stripping techniques),
- cutting technique,
- specimen thickness,
- radioisotopic concentration,
- exposure time.

As for SEM determinations, the following points deserve a major attention:  
deposition of conductive material on the sample surface,

energy of the primary beam,  
incident angle of the primary beam.

In our experiments the resin initially in  $\text{Cl}^-$  form was gradually converted batchwise into  $\text{SO}_4^-$  form by prefixed contact time with 0.006N  $\text{Na}_2\text{SO}_4$  solutions containing various amounts ( $6.6\text{--}13.4 \mu\text{Ci}/\text{dm}^3$ ) of  $^{35}\text{S}$  ( $\beta$  emitter,  $E = 0.167 \text{ MeV}$ ,  $t_{0.5} = 87.2 \text{ d}$ ).

Few beads of each converted resin were then submitted to autoradiography by direct contact technique. This latter technique allows to operate in dry conditions and thus to avoid loss of the sulphate ion by hydrolysis of the ion-exchange resin.

After embedding and microtomizing, equatorial sections of the bead ( $35 \mu\text{m}$  thick) were exposed to an X-ray sensitive film (Kodak Min R) for different exposure times (24, 48, 72, 96 h) in a dark room.

Resins with a weaker consistency were embedded into a thermoplastic material ("Hot melt" from Budacolor, Hungary) and microtomized by a Reichert Jung Mod. 1130 microtome. Equatorial sections of glassy resins, previously embedded into araldite, were obtained by double erasure on an abrasive paper.

After prefixed exposure times, sensitized films were separated from specimens and processed at  $18^\circ\text{C}$  (5 min in Kodak D19 developing solution plus 5 min in Kodak F5 fixing bath). Each autoradiogram was then evaluated for its optical density on a microdensitometric system obtained with a Leitz Wetzlar light microscope equipped with a CdS exposimeter.

In fig. 1 the optical density of experimental autoradiogram from the resins investigated is shown as a function of the exposure time and isotope concentration in  $\text{Na}_2\text{SO}_4$  solution,

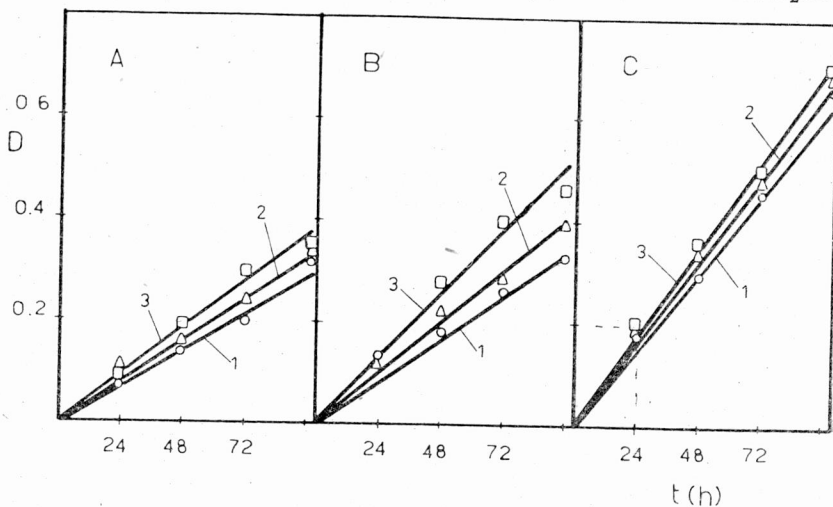


Fig. 1. Optical density versus exposure time at different radioisotope concentrations

A —  $6.7 \mu\text{Ci}/\text{dm}^3$ , B —  $10 \mu\text{Ci}/\text{dm}^3$ , C —  $13.4 \mu\text{Ci}/\text{dm}^3$ ; 1 — Amberlite IRA 458, 2 — Amberlite IRA 67, 3 — Kastel A102 anion-exchange resins

Rys. 1. Gęstość optyczna w zależności od czasu napromieniania przy różnych stężeniach radioizotopu  
A —  $6,7 \mu\text{Ci}/\text{dm}^3$ , B —  $10 \mu\text{Ci}/\text{dm}^3$ , C —  $13,4 \mu\text{Ci}/\text{dm}^3$ ; 1 — Amberlite IRA 458, 2 — Amberlite IRA 67, 3 — żywica anionitowa.  
Kastel A102

indicating the following Lambert-Beer type relationship:

$$D = \lg I_0/I = kCt, \quad (2)$$

where  $I_0$  and  $I$  — intensity of the emergent light from non-sensitized and sensitized regions of the film, respectively;  $k$  — proportionality factor ( $\text{dm}^3/\mu\text{Ci}, \text{h}$ );  $C$  — concentration of  $^{35}\text{S}$  in  $\text{Na}_2\text{SO}_4$  solution ( $\mu\text{Ci}/\text{dm}^3$ );  $t$  — exposure time (h).

Adopting a  $D = 0.2$  value as the minimum optical density to obtain a detectable track, exposure time of 24 h and isotope concentration around  $13.4 \mu\text{Ci}/\text{dm}^3$  were selected as operating conditions in this study.

Figure 2 shows a typical autoradiographic result from one of the resins investigated at different degree of conversion. As it can be seen a uniform distribution of sulphates throughout the resin bead during the  $\text{Cl} \rightarrow \text{SO}_4$  conversion appears. Accordingly the relatively unusual "progressive conversion model" mechanism for ion diffusion in that resin.

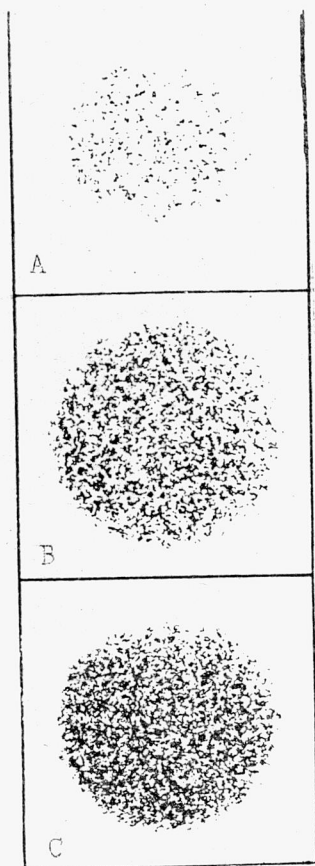


Fig. 2. Autoradiograms of  $35 \mu\text{m}$  sections of resin Kastel A102 activation —  $\text{Na}_2\text{SO}_4$  0,006 N,  $\text{pH}=3$  with  $^{35}\text{S}$  concentration =  $13.4 \mu\text{Ci}/\text{dm}^3$ ; emulsion — Kodak Min RX ray film; exposure time — 24 h; A  $\approx 33\%$  degree of conversion in  $\text{SO}_4^{2-}$  form; B  $\approx 66\%$  degree of conversion in  $\text{SO}_4$  form; C  $\sim 100\%$  degree of conversion in  $\text{SO}_4$  form

Rys. 2. Autoradiogramy  $35 \mu\text{m}$  przekrojów żywicy Kastel A102 aktywacja —  $\text{Na}_2\text{SO}_4$  0,006 n,  $\text{pH}=3$ , stężenie  $^{35}\text{S}=13,4 \mu\text{Ci}/\text{dm}^3$ ; emulsja — błona rentgenowska firmy Kodak; czas ekspozycji — 24 h; A  $\approx 33\%$  stopień konwersji w formie  $\text{SO}_4^{2-}$ ; B  $\approx 66\%$  stopień konwersji w formie  $\text{SO}_4$ ; C  $\approx 100\%$  stopień konwersji w formie  $\text{SO}_4$

200  $\mu\text{m}$

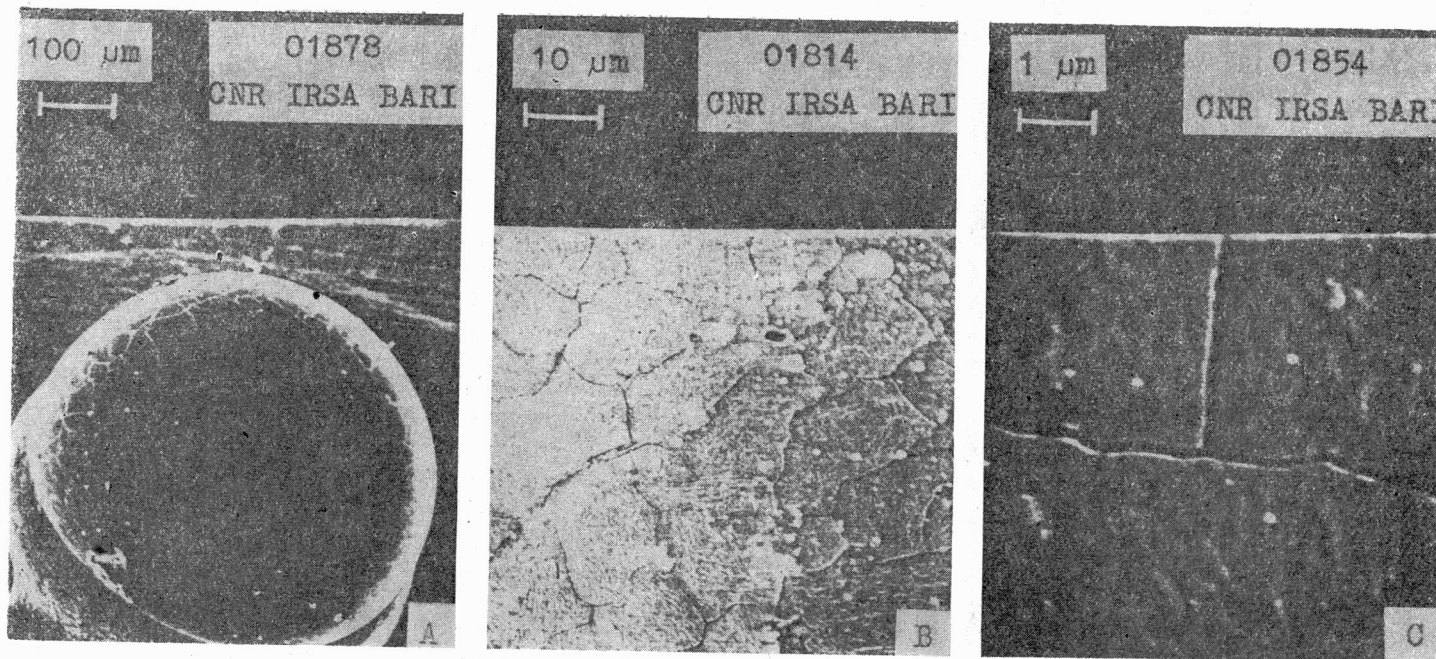


Fig. 3. Scanning electron microscope photographs of resin Kastel A102 (20 kV, graphite covering)

*A* — uncut resin bead ( $\times 100$ ), *B* — bead section ( $35 \mu\text{m}$ ) ( $\times 1\,000$ ), *C* — bead section ( $35 \mu\text{m}$ ) ( $\times 10\,000$ )

Rys. 3. Mikrofotografia żywicy Kastel A102 ze skaningowego mikroskopu elektronowego (20 kV, pokrycie grafitowe)

*A* — nieprzecięty paciorek żywicy ( $\times 100$ ), *B* — przekrój paciorka ( $35 \mu\text{m}$ ) ( $\times 1\,000$ ), *C* — przekrój paciorka ( $35 \mu\text{m}$ ) ( $\times 10\,000$ )

during the  $\text{Cl} \rightarrow \text{SO}_4$  exchange kinetics is unambiguously demonstrated by autoradiographic measurements.

Autoradiographed sections and single resin beads were also submitted to graphite covering, using an E12-E4 coater by Edwards, England, and rapidly inserted into the chamber of a scanning electron microscope (Stereoscan S4 by Cambridge Instrument Ltd, England). A maximum energy of electron beam of 20 kV prevented the modification of the graphitized resin bead. Optimal incidence angle of the beam had to be tentatively checked in each case.

As shown in fig. 3, surfaces of the single resin bead and its sections were clearly appreciated in these conditions. The thoroughly fractured morphology provides an explanation of ion diffusion pathways into the resin according to the progressive conversion model, supporting the conclusion drawn previously on the basis of autoradiographic results.

## 5. CONCLUSIONS

Autoradiography and scanning electron microscopy may improve significantly the fundamental knowledge of mass transport in ion-exchange and similar processes. By their combined application quite unusual conclusions were obtained on the ion diffusion mechanisms in the resin during the  $\text{Cl} \rightarrow \text{SO}_4$  ion-exchange, as an aspect of the sea water desulphation process.

The versatility and the relative simplicity of these techniques and the cheap cost of autoradiographic experiments deserve a wider extension to structural studies on polymeric materials such as ion exchangers, membranes, adsorbers, active carbon, etc. actually used in physicochemical treatments of water and wastewater.

However, apart from the need of expensive SEM equipment, it is difficult to have a general methodology for application of these techniques to various problems; optimal operating conditions have to be checked carefully in each application.

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#### BADANIE REAKTYWNYCH POLIMERÓW ZA POMOCĄ AUTORADIOGRAFII I MIKROSKOPII SKANINGOWEJ

W badaniach dyfuzyjnych nad reaktywnymi polimerami duży postęp wiedzy o transporcie masy można osiągnąć stosując autoradiografię i mikroskopię skaningową. Przedstawiono przegląd tych technik i ich zastosowanie do badań procesu odsiarczania słonawej wody morskiej.

#### UNTERSUCHUNG VON REAKTIVEN POLYMEREN MITTELS AUTORADIOGRAPHIE UND SCANNING-MIKROSKOPIE

Eine intensive Entwicklung der Wissenschaft in Hinsicht des Stofftransportes in Diffusionsversuchen von reaktiven Polymeren, kann bei der Anwendung der Autoradiographie und Scanning-Mikroskopie erzielt werden. Gegeben wird eine Übersicht dieser Techniken und deren Anwendung bei der Entschwefelung von salzigem Meerwasser.

#### ИСПЫТАНИЯ РЕАКЦИОННОСПОСОБНЫХ ПОЛИМЕРОВ С ПОМОЩЬЮ АВТОРАДИОГРАФИИ И СКАНИРОВАННОЙ МИКРОСКОПИИ

Большого прогресса в накоплении знаний о транспорте массы в диффузионных испытаниях по реакционноспособным полимерам можно достигнуть, применяя авторadiografiю и сканированную микроскопию. Представлен обзор этих техник и их применение для испытаний процесса обессеривания солоноватой морской воды.