TRISKEM INFOS
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SOMMAIRE

Edito:

We are very happy to announce that a key milestone of our C.L.I.P.S. 2020 project, the fabrication of 100kg of AMP-PAN, has been performed successfully. This fabrication run is a critical step on our path to the integration of a production unit allowing the fabrication of semi-industrial quantities (100s of kg to tons per year) of selective and economic PAN based resins e.g. for the decontamination of effluents. These resins are based on a platform technology allowing for the rapid and efficient development and production of selective resins for our customers decontamination needs. You will find more information in this newsletter.
This 21st TKI closes this very particular year 2020 with all its challenges and dramatic events - we wish you nevertheless a very good end of the year and happy holidays! Stay safe and healthy! As for the new year 2021…

We need Innovation more than ever!
Let 2021 be the year of Optimism, Enthusiasm and Innovation.
We will do our Best to reply to your needs and wish you Health, Happiness and Success in 2021.
Thank you very much for your Confidence, your Challenges and your Collaboration!

PAN Resins

Integration and upscale of in-house PAN Resin production.
Based on a several year long cooperation on the commercialisation of polyacrylnitrile (PAN) based resins such as AMP-PAN, KNiFC-PAN and MnO_2-PAN, which were originally developed and produced by Dr. Sebesta at the Czech Technical University in Prague (CVUT), TKI were able to develop a process which allows to produce PAN based selective resins in semi-industrial quantities. This development was instigated by the aim of producing already commercially available PAN resins in-house in elevated quantities and in an eco-responsible way, as well as developing new PAN based resins to satisfy existing and future market needs. These objectives are currently being realized via a structuring project called C.L.I.P.S. 2020, which is described further below in this newsletter.

PAN Resins.
The use of polymers such as PAN to enmesh very fine particles of selective inorganic compounds was introduced by Sebesta et al. (1). Sebesta and co-workers produced and tested a wide range of different inorganic and organic compounds (1, 2) by embedding them into a PAN polymer matrix resulting in mechanically stable particles of well-defined particle size. The highly porous and hydrophilic polymer matrix allows for obtaining fast kinetics, while high load of the selective compounds (up to 85% with respect to employed amount of PAN) allows for elevated capacity for the respectively targeted elements. They could show that a variety of compounds covering a wide range of different selectivities may be encapsulated using PAN (1).

The most widely used inorganic compound in this context is ammonium phosphomolybdate (also Ammonium MolybdoPhosphate, AMP) an inorganic cation exchanger known for its high selectivity for Cs over a wide range of conditions and on which the AMP-PAN resin is based. Sebesta et al. could indeed show that the AMP-PAN resin is, in terms of kinetics and Cs capacity, similar to pure AMP (3).

Typical applications of the AMP-PAN resin include:

The determination of Cs-134/7 in natural water samples, with particular focus on sea water samples, this is especially true in the wake of the Fukushima accident. It could be shown by Kamenik et el. (4) e.g. that Cs may be concentrated from 100L of acidified seawater on 25 mL AMP-PAN columns in less than 6h upfront to gamma spectrometry measurements allowing to obtain minimum detectable activities (MDA) as low as 0.15 $Bq.m^{-3}$ for Cs-137 and 0.18 $Bq.m^{-3}$ for Cs-134 with high chemical yields in the order of 90% (determined via ICP-MS using stable Cs).

Further to its use in gamma spectrometry the AMP-PAN resin has also been used by several groups (5, 6) for the determination of Cs-135, and Cs-137, by mass spectrometry. The Cs isotopes are typically first retained, and thus concentrated, on the AMP-PAN resin while matrix elements and isobaric interferences pass through.

Figure 1: Sample of AMP-PAN produced employing the semi-industrial production unit

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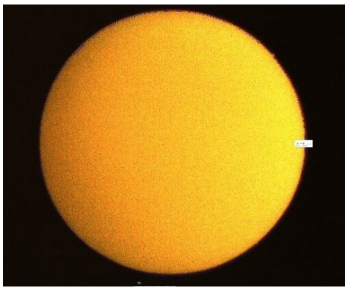

Figure 2: microscope image of an AMP-PAN bead

Cs is then typically eluted using $NH_3{\cdot}H_2O$ of elevated concentration (e.g. 1.5M) and further purified using anion exchange and cation exchange resulting in excellent purification of Cs allowing its quantification via e.g. ICP-MS/MS or TIMS.

Another application of the AMP-PAN resin is the removal of high levels of Cs-137 from highly active samples upfront to their analysis e.g. via alpha or mass spectrometry (7).

Besides analytical applications AMP-PAN resin has also been employed, with respect to its fast kinetics, high capacity and high chemical and radiolysis stability (no deterioration after exposure to up to 10^6 Gy) for the treatment of radioactively contaminated effluents and waste solutions (8).

Brewer et al. (9) could show employing very small columns (1.5 mL) that AMP-PAN was able to remove Cs from highly radioactive acidic liquid waste with high decontamination factors (>3000). In a follow-up project (10) they successfully upscaled this application to 45L of simulated acidic liquid radioactive waste containing high amounts of cesium (130 mg/L), potassium and sodium. Two consecutive 60 mL AMP-PAN columns followed by a third 'polishing' column (220 mL AMP-PAN) were employed to successfully prove the concept of Cs removal from liquid waste samples.

The PAN polymer is based on the CHON principle (it only contains Carbon, Hydrogen, Oxygen, and Nitrogen) it is thus suitable for incineration as it will not produce ash. It could further be shown that PAN based resins may be immobilized in cement or vitrified (1).

As shown in the examples above, PAN embedded inorganic compounds, particularly AMP-PAN are very versatile tools for use in analytical applications as well as for the decontamination of effluents. Especially the latter application is, with respect to the increasing number of nuclear installations undergoing decommissioning, gaining importance. To help its users meeting these challenges, TrisKem took the decision to set-up a semi-industrial production unit allowing to produce elevated amounts of these types of selective resins.

C.L.I.P.S. 2020

In 2018 TKI started a structuring project called "C.L.I.P.S 2020" with the aim of integrating a platform technology to its production portfolio allowing for the rapid development and production of new PAN based resins according to our customers needs and requests. A second aim was setting-up an installation allowing for the semi-industrial production of several hundreds of kg to tons of such resins per year using an optimized and eco-friendly process (use of non-dangerous solvents, strongly limiting the amount of water employed during the production process,…).

This project was elected as one of the laureates of the "Concours d'innovation 2018, 1ère vague: des projets innovants d'envergure" by the BPI (French Bank for the investment in the Future). Further to the BPI, the Region of Brittany and Rennes Metropole also financially supported this project.

News:

1st Virtual User Group Meeting

Our very first virtual and worldwide Users Group Meeting took place on the 24th of November as part of the vCARM conference (**https://www.npl.co.uk/events/vcarm-2020**) organized by the National Physical Laboratory (NPL). With 12 presentations held by presenters from institutes from 9 different countries (from Canada to Australia) it was truly a worldwide meeting. With a peak at 105 participants connected at the same time, and 147 participants overall, the high quality of the presentations covering a wide range of topics such as environmental monitoring, decommissioning, decontamination, metallomics and radiopharmacy, vivid discussions - through direct questions or the chat – and your kind and very positive feedback we esteem that the meeting has been a great success!
Our warmest thanks to Ben Russel and the NPL Events team, all presenters, and all participants!

You will find the slides presented at the vUGM here: **https://www.triskem-international.com/virtual-users-group-meeting-2020.php**.

We are currently evaluating the possibility of having such a virtual meeting once per year. Please do not hesitate to send us your thoughts on this to **shappel@triskem.fr.**

In a first step a small-scale production installation was set-up and validated allowing for the fabrication of analytical grade PAN resins (particle size 100 – 600 µm) at a rate of several kg per day.

Initial tests indicated that the in-house produced AMP-PAN resin indeed showed high Cs retention, selectivity and fast kinetics, as is shown exemplarily in the graph below.

Accordingly, several batches of AMP-PAN (4 batches) and KNiFC-PAN (3 batches) resins produced in-house using this set-up were validated against reference batches of both resins produced by the CVUT. It could be shown that AMP-PAN and KNiFC-PAN resins produced at Triskem show very similar performance compared to CVUT produced batches: for all tested batches (AMP-PAN and KNIFC-PAN) >99% of Cs were retained on the tested columns under the given test conditions (based on the respective CVUT CoA). No significant difference was observed. The same is true for the dynamic Cs capacity of the AMP-PAN and the KNiFC-PAN resins. Within given uncertainties both the TrisKem and the CVUT produced resins show no significant difference in terms of dynamic capacity. The respective validation folders are available upon request also supported this project financially.

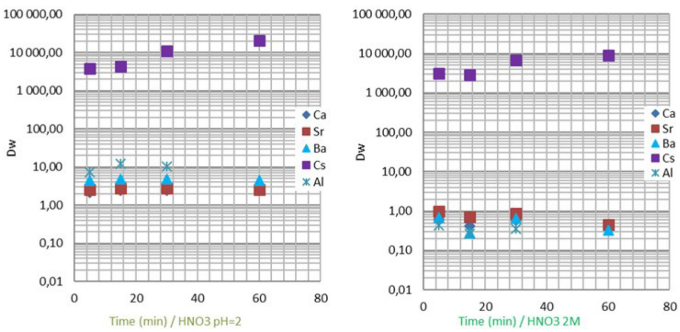

Figure 3: D_w of selected elements at varying contact times, 0.01M HNO_3 and 2M HNO_3

Fig. 4 shows the particle size distribution typically obtained at Triskem during the production of 100 – 600µm AMP-PAN particles. In the shown example the D_{10} is 131 µm, the D_{50}[1] is 242 µm and the D_{90} is 443 µm, while the uniformity coefficient Uc (D_{60}/D_{10}) is in the order of 2.1. Similar results were obtained for KNiFC-PAN.

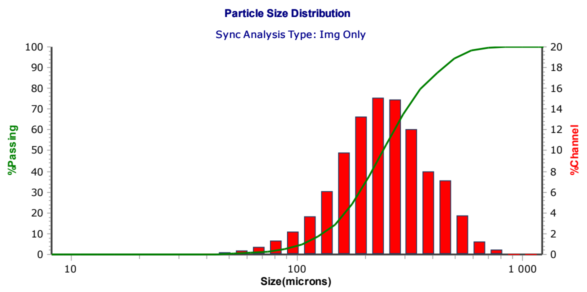

Figure 4: particle size distribution, TKI AMP-PAN, 100 – 600 µm

It was concluded that both AMP-PAN and KNiFC-PAN resins produced via this new set-up were showing a performance comparable to that of already commercialized PAN resin batches produced by the CVUT and having a suitable particle size distribution.

Accordingly, all new batches of both resins sold by Triskem will now be produced in-house.

Further a second, 'semi-industrial' installation has just been implemented - currently allowing to produce 20kg per day of 1000µm AMP-PAN beads. This setup was successfully tested via the production of 100kg of AMP-PAN resin over 5 consecutive days at a rate of 20kg per day.

Fig. 5 shows typically observed particle size distributions (representative samples taken at the end of the first day and of the last day respectively). Overall the five consecutive 20kg production runs resulted in a very reproducible mean particle size distribution with a D_{50} of 953 µm ± 4.0% (N=5, k=1) and a narrow mean particle size distribution with a Uc of 1.2 ± 4.6% (N=5, k=1) and high sphericity of ~97%.

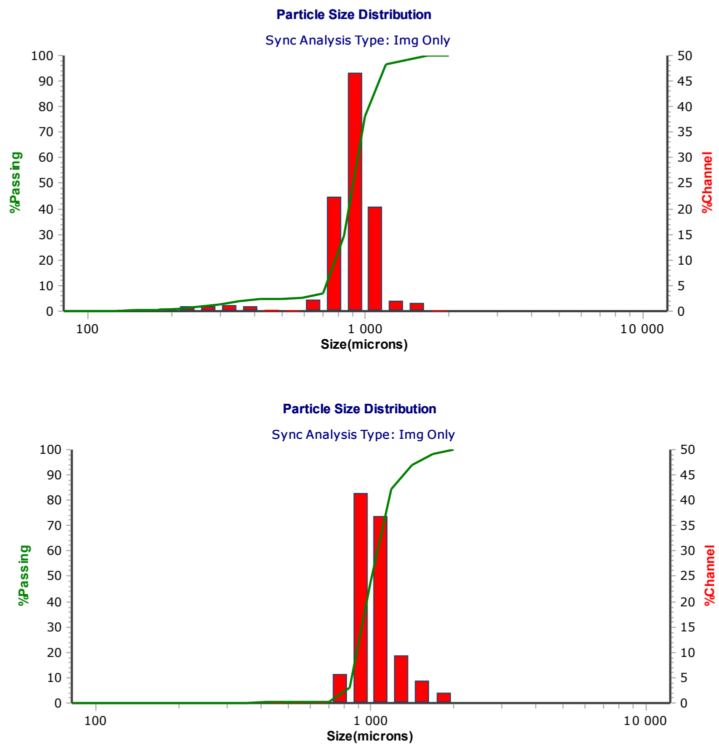

Figure 5: particle size distribution, TKI AMP-PAN 100kg production run, first and last day

It is also very important to note that, in addition to the fact that up to 20kg of AMP-PAN per day could be produced in a stable and reproducible quality, this production was performed avoiding the use of dangerous or corrosive solvents. Further the amount of water used during this production process could be reduced by up to 90% compared to the original process. Both aspects are very important with respect to our aim of making the in-house production, including the semi-industrial production, eco-responsible.

The process will be upscaled further in the coming months.

[1]D_{50} = 50% of the particles detected by the system were ≤ 242 µm

As indicated before, one main aim of the C.L.I.P.S 2020 project is developing new resins based on its platform technology, this is concerning inorganic compounds such as ZrP, TiO_2/HTiO, PAA,… as well as organic compounds such as TBP, HDEHP,…

These new resins, like the AMP-PAN, are mainly destined for use in the decontamination of radioactively contaminated effluents from nuclear industry and decommissioning (e.g. for removal of isotopes of Sr, Ni, Co,…), nuclear medicine departments, mining effluents, NORM industries… as well as to the valorisation and recovery of high-value elements such as Mo, REE, Sc,… originating from mining, recycling, nuclear and non-nuclear industries.

Further to new inorganic compounds the use of different polymers is currently being evaluated, in function of the effluent to be treated (e.g. the use of PES for highly alkaline effluents).

If you are interested in obtaining more information, or if you have an existing separation or decontamination project, please do not hesitate to contact us!

Figure 6: Sample of AMP-PAN produced employing the semi-industrial production unit

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