17TH EUROPEAN MEETING ON SUPERCRITICAL FLUIDS

TH EUROPEAN MEETING HIGH PRESSURE TECHNOLOGY

Institute of Chemical and Environmental Technology (ITQUIMA) APRIL 8 - 11, 2019

PROGRAMME





Falk, Ramon González, Elisabet González-Mira, Santi Sala, Nora Ventosa, and Alba Córdoba*. Nanomol Technologies SL.

Supercritical antisolvent coprecipitation in the pharmaceutical field:different polymers 80 for different drug release. Iolanda De Marco*, Paola Franco, Ernesto Reverchon. University of Salerno.

Supercritical CO₂ process to extract Cerium using CO₂-phile extractant. S. Bouali^{*}, G. 82 Toquer, A. Leybros, A. Leydier, A. Grandjean, T. Zemb. CEA, DEN, DE2D, SEAD, LPSD, F30207.

Supercritical fluid extraction of rare earth elements from nitric acid solutions. Khavaza 84 T.N.*, Tokpayev R.R., Atchabarova A.A., Beknazarov K.I., Zlobina E.V., Nauryzbayev M.K. Al-Farabi Kazakh National University.

A model for supercritical-fluid extraction of rare earth elements from phosphogypsum 86 leaching solutions. Tokpayev R.R*., Khavaza T.N., Atchabarova A.A., Beknazarov K.I., Nefedov A.N., Nauryzbayev M.K. Al-Farabi Kazakh National University.

SESSION 4. 12:00 – 13:00

Supercritical Assisted Atomization process for the production of antitumoral active 89 principle-polysaccharide microspheres. Alessia Di Capua*, Renata Adami, Ernesto Reverchon. University of Salerno.

Use of Subcritical Water Technology to Develop Cassava Starch/Chitosan Bioactive 91 Films Reinforced with Cellulose Nanofibers. Yujia Zhao, Raquel Razzera Huerta, Marleny D.A. Saldaña*. University of Alberta.

Thymol release kinetics of PLA-based foams and films obtained by using supercritical 94 *CO*₂. Jasna Ivanovic*, Stoja Milovanovic, Ivana Lukic, Robert Kuska, Sulamith Frerich. University of Belgrade.

*Functionalization of PLA with coumarin via click chemistry in scCO*₂. E. Gracia*, I. 96 Gracia, M.T. García, J.F. Rodríguez, A. De Lucas. University of Castilla La Mancha.

Subcritical Water Extraction of Phytochemicals from Allium hookeri Root and their 98 Antioxidant and Anticancer Effects. Aye Aye Myint, Youn-Woo Lee*, Jaehoon Kima*. Sungkyunkwan University.

Extraction of Oil from Black Fractionation Of Red Wine Grape Pomace By Subcritical 100 *Water Extraction/Hydrolysis and White Chia Seeds with subcritical n-propane.* Maša Knez Hrnčič*, Darija Cör, Željko Knez. University of Maribor.

Fractionation Of Red Wine Grape Pomace By Subcritical Water Extraction/Hydrolysis. 102 Bruno Pedras, Isabel Sá-Nogueira, Pedro Simões, Susana Barreiros, Alexandre Paiva*. Universidade Nova de Lisboa.

Assessment of Phoenix dactylifera Fruits (Date Palm) by using super and subcritical 103 *fluid.* S. Jazi, A. Elmi Kashtiban, A. Cherif, W. Mnif, J.A Mendiola, E. Ibañez. Institute of Food Science Research (CIAL-CSIC).

Lignin liquefaction in supercritical ethanol with suppressing solvent consumption. 105 Jaehoon Kim*, Asim Riaz, Deepak Vermaa, Jeong Hyeon Lee, Jin Chul Kim, Sang Kyu Kwak. Sungkyunkwan University.

Exploring CO_2 geological storage mechanisms at the pore scale using microfluidics 107 approaches. Anaïs Cario, Yves Garrabos, Carole Lecoutre, Olivier Nguyen, Samuel Marre*. Univ. Bordeaux.

Supercritical fluid extraction of rare earth elements from nitric acid solutions

Khavaza T.N.*, Tokpayev R.R., Atchabarova A.A., Beknazarov K.I., Zlobina E.V.,

Nauryzbayev M.K.

Center of Physical Chemical Methods of Research and Analysis of Al-Farabi Kazakh National University, 050012, Almaty, Republic of Kazakhstan

*Corresponding author: <u>k.tamina@mail.ru</u>

1. Introduction

Today, the actual problem is the search and processing of rare-earth raw materials for the production of pure metals, including their extraction from secondary raw materials. One of the promising sources of raw materials is phosphogypsum - a large-tonnage waste from the industrial production of phosphoric acid, the mass content of rare-earth metals can reach 0,5 %. In the phosphogypsum obtained at the "Mineral Fertilizers" LLP, (Zhambyl region, Kazakhstan), the prevailing REEs are yttrium 82.9 g/t, lanthanum 44.1 g/t, cerium 40.2 g/t, neodymium 36.9 g/t. The use of supercritical fluid extraction makes it possible to improve the process of extracting these metals from hard-to-recover raw materials in comparison with previously known heap leaching methods, and also provides a transition to a real green economy. The aim of the research is the development of highly efficient, energy-saving supercritical technologies for processing raw materials and industrial wastes for extracting rare-earth metals. In this work, we studied the kinetics of extraction of Y from Y_2O_3 with TBP-HNO₃ and DEPHA-HNO₃ complexes in supercritical carbon dioxide.

2. Results and discussion

The model system included yttrium oxide, nitric acid, TBP and DEHPA. In the cell for extraction, containing a portion of 0.1119 g of yttrium oxide with a particle size of 0.03 mm, was added nitric acid with a concentration of 3.5 mol/l, and an organic extractant in a ratio W:O = 10:1. The flow rate of SC-CO₂ was 20 ml/min. The concentrations of TBP and DEHPA in SC-CO₂ were 3% by weight, the temperature in the system was 318 K, and pressure was 20 MPa. From the literature data, it was found that the solubility of the organic extractant increases with increasing pressure and decreasing temperature¹. Also, the extraction of REEs proceeds most fully when using nitric acid and organic extractants². The yttrium concentration in the system was determined by the amount of yttrium concentration in the CO₂ eluate. The results are presented in Fig. 1.



Figure 1. Change of reaction rate constant depending on extraction time

Processing of the results presented in Fig. 1 was carried out according to³. The extraction effiency E can be expressed as

$$E = \frac{c_{A0} - c_A}{c_{A0}}$$

where $C_{A0} = 0.1190 \text{ g} / 1$ and $C_A = C_{A0} - C(t)$ is the residue of yttrium oxide in the reactor.

As a result, the rate constant of yttrium extraction from yttrium oxide in the presence of TBP was obtained which was 5×10^{-5} min⁻¹, and for the process of yttrium extraction in the presence of DEHPA it was 7×10^{-4} min⁻¹.

3. Conclusions

To establish the optimal conditions for the SF extraction of REEs from phosphogypsum, yttrium was extracted from a model solution in the presence of TBP and DEHPA. Therefore, it was proposed to use DEHPA as a co-extractor of rare-earth metals from phosphogypsum (Zhambyl region, Kazakhstan) with sc-CO₂. Optimal leaching and extraction conditions were obtained on model yttrium solutions (pH, Cex, W:O), which were used for extraction under supercritical conditions.

References

1. B.F. Myasoyedov, etc al. Supercritical Fluid Extraction of Radionuclides // Supercritical Fluids: Theory and Practice. - 2007. - V.2. - #3. - P. 5-24.

2. M.D Samsonov, etc al. Supercritical fluid extraction of rare earth elements thorium and uranium from monazite concentrate and phosphogypsum using carbon dioxide containing tributyl phosphate and di- (2-ethylhexyl) phosphoric acid // Supercritical fluids: Theory and practice. - 2015. - V.10. - #2. - P. 40-50.

3. ZHU Liyang et al. Kinetics of reactive extraction of Nd from Nd_2O_3 with TBP-HNO₃ complex in supercritical carbon dioxide // Chinese Journal of Chemical Engineering. – 2009. – V.17. – #2. – P. 214-218.