Physicochem. Probl. Miner. Process. 50(1), 2013, 387−397

Physicochemical Problems
of Mineral Processing

www.minproc.pwr.wroc.pl/journal/

ISSN 1643-1049 (print)
ISSN 2084-4735 (online)

Received May 29, 2013; reviewed; accepted August 11, 2013

A STUDY OF SELECTED PROPERTIES OF RHENIUM SULPHIDE DISPERSION

Dariusz W. PAWLAK[*], Jozef L. PARUS[*], Ewa SKWAREK[*], Wladyslaw JANUSZ[**]

[*] Radioisotope Centre POLATOM, National Centre for Nuclear Research, Otwock, Poland
[**] Maria Curie Sklodowska University, Pl. M. Curie Sklodowskiej 3, 20-031 Lublin, Poland
wladyslaw.janusz@umcs.lublin. pl

Abstract: Due to potential application of rhenium sulphide in medicine and industry, this study is focused on the properties of synthetic and commercial rhenium sulphide. The main reaction of rhenium sulphide preparation involves potassium perrhenate and sodium thiosulphate in the acidic environment giving a mixture of rhenium sulphide and sulphur. The next step is removing sulphur by its dissolution in ether. Stabilization by Povidone K-25 is needed to obtain rhenium sulphide dispersed with the grain size of 0.5–4 μm. The extrapolated value of pHiep for synthesised rhenium sulphide is 2.3 whereas for commercial samples this value is lower than 2. For synthetic sample a dependence of zeta potential on the carrier electrolyte concentration is found. It is larger than that for the commercial sample, probably due to surface oxidation during synthesis or purification.

Keywords: *rhenium sulphide, particle size distribution, zeta potential*

Introduction

The method of rhenium sulphide preparation and its properties are studied in relation to its potential application in nuclear medicine as a catalysts in hydrogenation, hydrodesulphurization, hydronitriding (Klett et al., 2007, De Los Reyes, 2007) as well as in the form of nanoparticles in electronics (Coleman et al., 2002). Rhenium sulphide is the most common carrier of radioactive rhenium in nuclear medicine (Junfeng et al., 2007). Though there have been developed a number of procedures for sulphide preparation, they produce rhenium sulphides of different structures which is still the subject of studies.

Traore described preparation of Re_2S_7 using the acidified solution of potassium perrhenate and thiosulphate or hydrogen sulphide (Escalona et al., 2007). After annealing at 110 °C for a few days, the obtained black precipitate was identified as

http://dx.doi.org/10.5277/ppmp140132

Re_2S_7 of the tetragonal structure. According to the authors, this sulphide can be readily decomposed in hydrogen atmosphere to give amorphous rhenium trisulphide, ReS_3, which is a precursor of rhenium disulphide, ReS_2. It can be obtained in vacuum at high temperature as the reaction product of metallic rhenium and elementary sulphur. It is regarded as the most stable rhenium sulphide. It has a hexagonal structure (a = 3.14 and c = 12.2 Å), but its parameters can differ insignificantly depending on the excess of sulphur.

Amorphous Re_2S_7 was also obtained in the reaction of potassium perrhenate and sodium thiosulphate in the acidic medium and studied by means of X-ray adsorption XAS method. The results showed that it has the rhombic cluster with metal-metal combination as a basic unit of the structure (Hibble et al., 1996).

The studies carried out by Schwarz et al. (2004) on the ReS_4, Re_2S_7, ReS_2 characteristics indicate the presence of sulphur in the forms S^{2-} and $S^{2-}{}_2$ in the compounds ReS_4 and Re_2S_7 whereby the content of S_2^{2-} in both ReS_4 and Re_2S_7 is larger than that in S^{2-}.The authors also suggest that the phases ReS_4 and Re_2S_7 are closely structurally connected. Given the fact that both sulphides transform into ReS_2 during heating, they proposed to treat them as components of the continuous structure $ReS_{1.5\text{-}1}(S_2)_{1\text{-}1.5}$ which differs in the S_2^{2-}/S^2 ratio.

Startsev et al. (1996) described the preparation of ReS_2 by means of the reaction of $HReO_4$ with H_2S at 450°C. The TEM studies revealed the presence of spheres of a diameter ~ 6 Å which is consistent with the inner distance d_{002} = 6.1 Å in the ReS_2 structure. However, the studies using the X-ray diffraction method showed that the structure is strongly disordered. Similarly, spherical ReS_2 particles of the size 0.1 do 1 μm were obtained as a result of the reaction of $ReCl_4$ with Li_2S in ethyl acetate. The XRD studies confirmed partially crystalline structure of the obtained substance.

For the purpose of the use in radiosynovectomy some attempts were made to synthesize colloidal rhenium sulphide based on the reaction of potassium perrhenate solution with thiosulphate solution in the acid medium (Junfeng et al., 1999) or using the method described by Tui and Denizot (Tu et al., 2007) in which the reagents (sodium thiosulphate and potassium perrhenate) were added in the solid state to the ethyl glycol/ethanol/distilled water mixture.

Though ReS_2 was investigated by many scientists, its structure is still studied. Murray et al. (1994) claim that ReS_2 has a triclinic crystalline structure and the elementary cell is characterized by the parameters: a = 6.417 Å, b = 6.510 Å, c = 6.461 Å, α = 121.10°, β = 88.38°, γ = 106.47°. The structure described by the authors is composed of asymmetric elementary cells with almost hexagonal, closed and packed layers.

In this paper the electrokinetic properties, particle size distribution and FTIR study of rhenium sulphide dispersions are presented. The electrokinetic properties as a function of pH reflect acid base properties of surface groups that may be interesting for catalytic behaviour of this compound (Stelzer et al., 2005). Moreover, the study of the particle size distribution of the rhenium sulphide suspension in the presence of gelatin and Povidon K-25 can be interesting for pharmaceutical applications in the radiosynovectomy.

Experimental

Materials and methods

The studies were carried out using a commercial Re_2S_7 sample purchased from Alfa Asear and the rhenium sulphide sample prepared according to the Jungfeng et al. procedure. The XRD analysis of the commercial Re_2S_7 showed its amorphous structure. The synthesis performed according to the Jungfeng et al. (1999) procedure confirmed that the concentration ratio of the solutions, $Na_2S_2O_3$:$KReO_4$ = 70:1 at the concentrations of $C_{Na2S2O3}$ equal to 0.0394 M and C_{KreO4} to 0.000563 M, and the heating time 30 min is optimal. Using this procedure the synthesis was repeated many times to determine the sulphur content in the samples and to remove elementary sulphur.

Methods of measurements

Measurement of particle size distribution was made using the Mastersizer 2000 apparatus (Malvern) with the hydro 2000μP (A) unit. The suspension containing 0.05 g sample in 50 ml of water was transferred to the measuring cell. The rate of suspension flow through the measuring cell was chosen adjusting the rotation speed of the pump and ultrasound intensity.

Distribution of sulphide particle sizes after washing the sample in the aqueous medium and dispersion subjected to stabilization using gelatin and Povidone K-25 were measured.

Zeta potential measurements of NaCl solution of the concentrations of 1, 10^{-1}, 10^{-2}, 10^{-3}M NaCl were made using the Zetasizer 3000 apparatus (Malvern). 0.02 g of commercial rhenium sulphide was added to the solution of a given concentration and subjected to dispersion using the ultrasound probe Sonicator XL 2020 (Misonix). Then, the suspension was transferred into 125 ml flasks, and pH was adjusted in the range from 3 to 9 in the presence of nitrogen using 0.1 M HCl and NaOH solutions. Four measurments of zeta potential were made for each solution. Infrared spectra were registered by means of the FTIR spectrometer Nicolet 8700A with the smart Orbit TR diamond ATR module.

Results and discussion

Specific surface area of Re_2S_7

As follows from the characteristics of the surface area of rhenium sulphide samples in Table 1, the studied samples have a similar specific surface area determined by the

BET method, whereas the synthetic samples are characterized by a slightly larger pore volume and larger average pore radius.

Table 1. Chracteristics of the specific surface area and porosity of the commercial and synthetic rhenium sulphides

Rhenium sulphide	Commercial.	Synthetic
Surface area from the BET isotherm [m^2/g]	5.18	6.26
Surface area from the Langmuir isotherm [m^2/g]	7.45	9.11
Total pore volume from adsorption 1.7 nm < *d* < and 300 nm diameter calculated by means of the BJH method [cm^3/g]	0.025	0.018
Total pore volume from desorption 1.7 nm < *d* < and 300 nm diameter calculated by means of the BJH method [cm^3/g]	0.025	0.0185
Average pore radius from adsorption – BJH method [nm]	17.86	12.9
Average pore radius from desorption – BJH method [nm]	16.1	10.5

Measurement of particle sizes

As follows from the comparison of Re_2S_7 particle size distribution before and after the ultrasound treatment, the commercial sample contains a large number of aggregates of different particle sizes from 1 to 1000 μm whereby the fraction >30μm in the sample not subjected to the ultrasound treatment is predominant. Treating the sample with ultrasounds for 6 min causes its unification and the particle size is from 0.2 to 2 μm (Fig. 1). Both numerical and volumetric distributions indicate monomodal particle distribution. The numerical distribution is characterized by: *d*(0.1) = 0.27 μm, *d*(0.5) = 0.40 μm and *d*(0.9) = 0.73 μm.

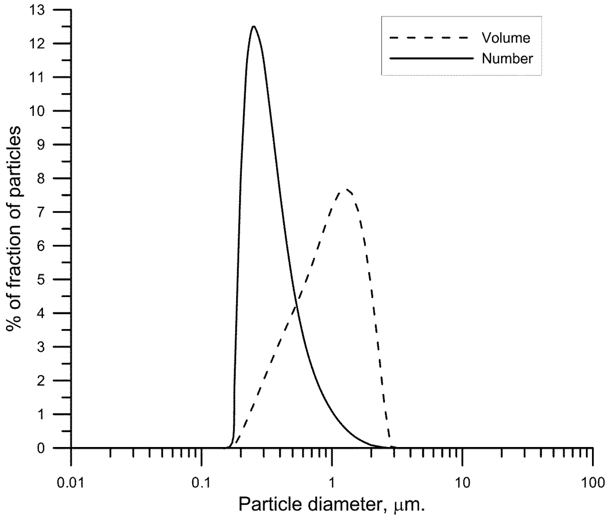

Fig. 1. Volumetric and numerical particle size distribution of the commercial sample Re_2S_7 after the six-minute ultrasound action

Figure 2 presents the volumetric particle size distribution of rhenium sulphide synthesized according to the Junfeng et al. procedure. As can be seen the radius of particles is from 3 to 50 μm. Because during the Junfeng et al. (1999) synthesis of rhenium sulphide the precipitation of elementary sulphur takes place and kinetics of precipitation of rhenium sulphide and sulphur is fast, so it is difficult to control the precipitation process. In the following experiments sulphur was removed by dissolution in ether. In several runs 1.16 g of precipitate was produced and it was washed with 400ml of ether. From the mass loss (0.5731 g) it was calculated that the content of elementary sulphur in the sample was 49%. After sulphur removal the rhenium sulphide sample was subjected to the particle size analysis (Fig. 2).

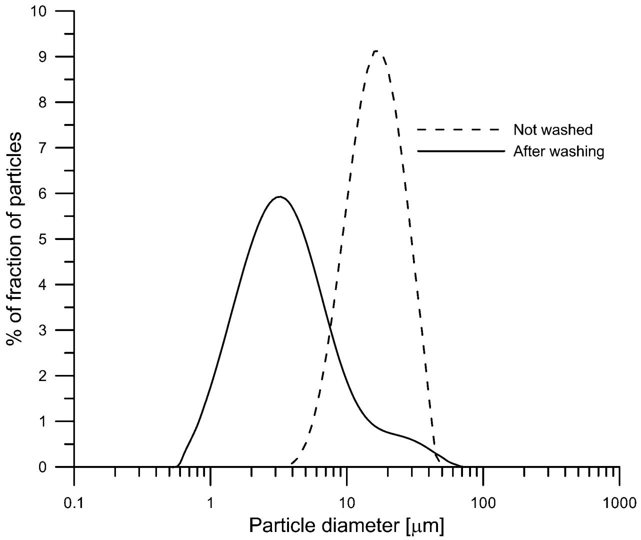

Fig. 2. Particle size distribution of the rhenium sulphide sample after sulphur washing

Table 2. Quantities characterizing the particle size distribution of the rhenium sulphide sample after washing with ether and stabilized with the pharmaceutical gelatine solution (2.3 mg/ml)

V ml	Dose mg/g	*d*(0.1) μm	*d*(0.5) μm	*d*(0.9) μm
0	0	1.27	3.24	10.62
3	138	1.09	2.43	6.62
6	276	0.84	1.76	3.74
10	460	2.62	91.66	162.5
20	920	0.86	2.02	18.08

Washing the obtained precipitate with ether changed the grain size distribution increasing the contribution of smaller aglomerates. Repetition of syntheses and washings with ether resulted in similar distribution of grain size as shown in Fig. 2.

Analyzing the particle size distribution in Fig. 3 and the quantities characterizing the particle size distribution in Table 2 one can see that the optimal dose for suspension stabilization is 276 mg/g. When this dose is larger the steric aggregation process is observed. When it is lower the gelatine stabilization process is not sufficiently efficient.

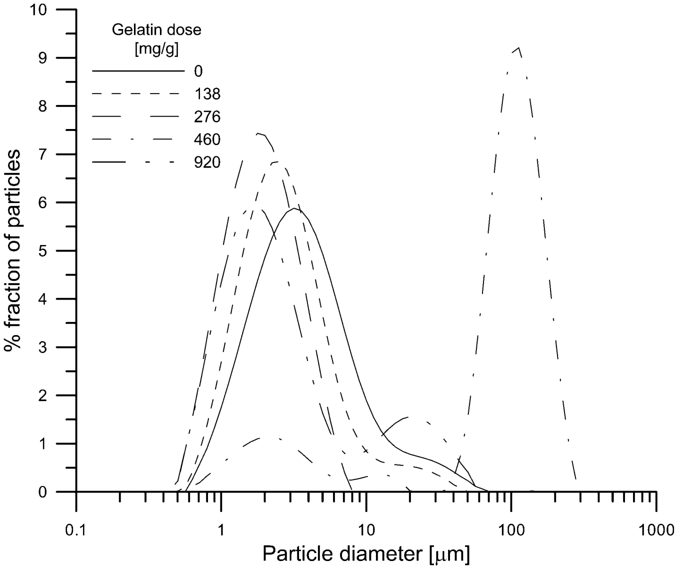

Fig. 3. Particle size distribution of the rhenium sulphide sample stabilized with gelatine

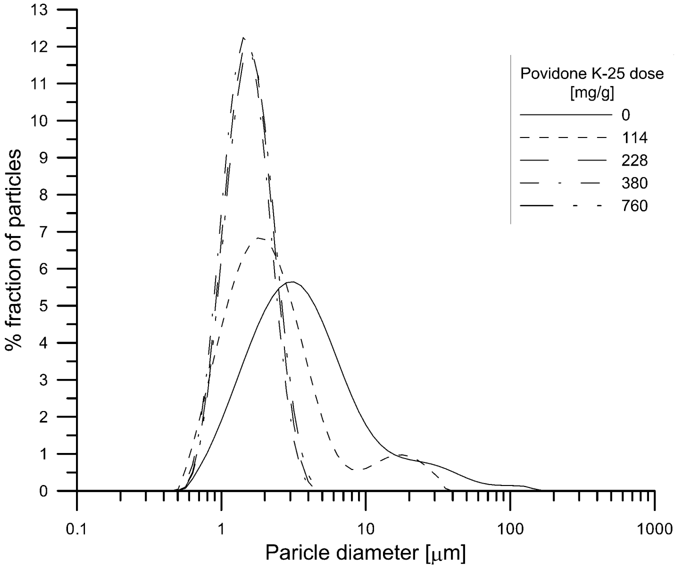

Fig. 4. Particle size distribution of the rhenium sulphide sample stabilized with Povidone K-25

Table 3. Quantities characterizing particle size distribution of rhenium sulphide sample after washing with ether and stabilizing with Povidone K-25 (1.9 mg/ml)

V [ml]	Dose mg/g	d (0.1) μm	d (0.5) μm	d (0.9) μm
0	0	1.27	3.24	10.62
3	114	0.89	1.92	6.62
6	228	0.90	1.44	2.31
10	380	0.87	1.39	2.21
20	760	0.92	1.48	2.39

Application of 228 mg/g dose of the Povidone K-25 resulted in the shift of suspension particle size distribution towards smaller particle size, d (0.5) = 1.4 μm. Like for gelatine, this dose was sufficient for dispersion of rhenium sulphite aggregates due to steric stabilization. However, compared to other stabilizers the essential difference was that successive increase in the Povidone K-25 dose did not cause suspension destabilization and the obtained particle size distribution of the sample remained unchanged.

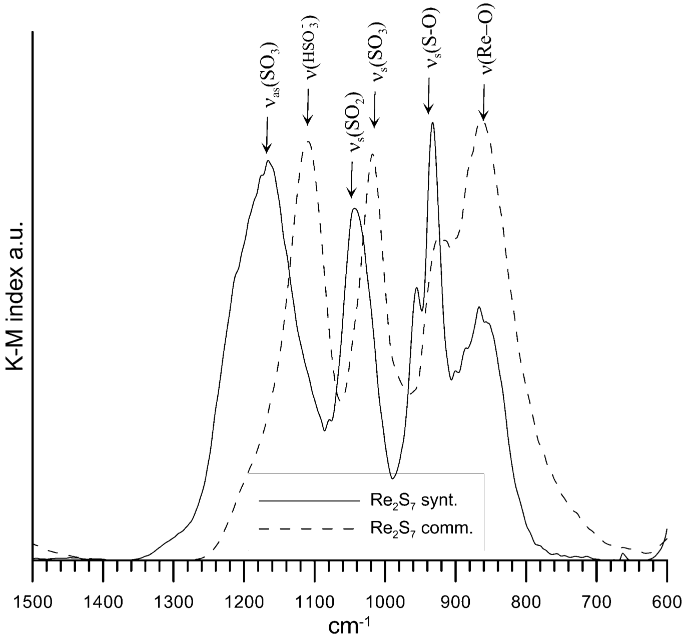

Fig 5. FTIR spectra of rhenium sulphide samples

Figure 5 presents the FTIR ATR spectra of the commercial rhenium sulphide sample and the sample prepared by synthesis. The commercial sample is characterized by vibration bands at the wave numbers 1109.1, 1018.05, 922.5 and 863.25 cm^{-1}. The stretching vibrations (the bond Re-O) are responsible for the band at 863.25 cm^{-1} (Luo et al., 2004), whereas stretching (v) vibrations of hydrosulphite ions are responsible for the band at 1109.1 cm^{-1} (Herlinger and Long, 1969). The bands at 1018.05 and 922.5 cm^{-1} result from the stretching vibrations of S-O groups in $S_2O_5^{2-}$ (Townsend et al., 2012). In the case of the sample prepared by the synthesis, the bands at 1166.1 and 1042.05 cm^{-1} formed due to stretching bonds in the sulphate group are visible (Peak et al.,1999).

Zeta potential

Figure 6 presents the change of the zeta potential of the commercial rhenium sulphide as a function of pH and electrolyte concentrations. As can be seen the potential decreases with the increasing pH and the background electrolyte concentration. However, within the given background electrolyte concentration the difference in the zeta potential is only about 15 mV. It should be mentioned that for all concentrations the zeta potential is negative which is characteristic of most metal sulphides because sulphide surface is rather easily oxidized which results in the presence of acidic groups and low pH_{iep}. The point pH_{iep} determined by extrapolation from the dependence of zeta potential on pH has the value of about 2. A similar shape of zeta potential as a function of pH and electrolyte concentration was observed for the zinc sulphide/NaCl solution system (Zhang et al., 1995). The charge formation at the sulphide/solution interface comes from the acid-base reactions of the =SH and =ZnOH groups as well as desorption/adsorption of Zn^{2+} ions (Rönngren et al., 1991).

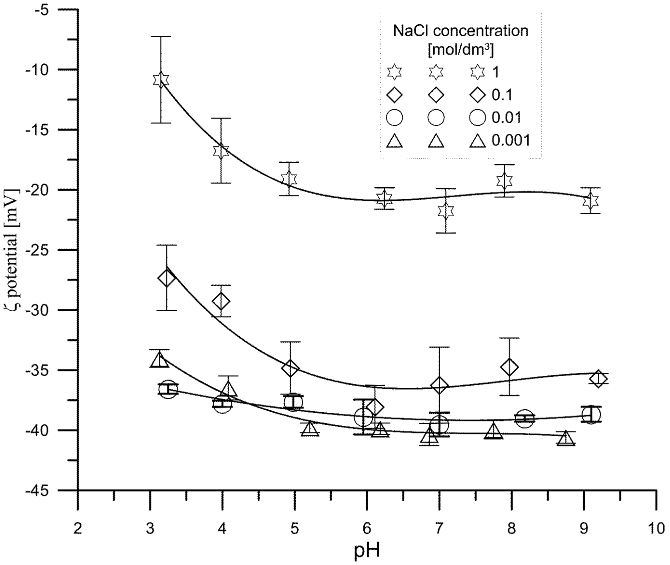

Fig. 6. Dependence of ζ potential of commercial rhenium sulphide in NaCl solutions as a function of pH

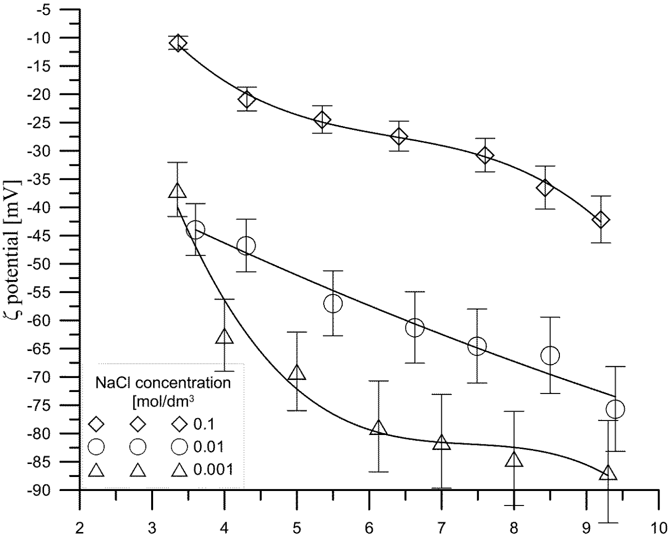

Fig. 7. Dependence of ζ potential of synthetic rhenium sulphide in NaCl solutions as a function of pH

Figure 7 presents the dependence of zeta potential of synthetic rhenium sulphide on pH in NaCl solutions of different background electrolyte concentrations. Like in the case of commercial rhenium sulphide the decrease in the zeta potential value with the increasing pH is observed. However, contrary to the commercial rhenium sulphide, the background electrolyte concentration in the case of the synthetic one has a stronger effect on the zeta potential value. In the case of the synthetic rhenium sulphide sample there were found surface sulphate groups (Fig. 5), formed due to oxidation of the sulphide surface, but sulphate ions can readily pass into the solution (Gärd et al., 1995). However, these ions can take part in the surface group complexation reaction and compete with the adsorption of background electrolyte ions. It was shown that copper sulphide oxidation results in the increasing zeta potential value as the hydrogen sulphate groups are replaced on the sulphide surface with the hydroxyl groups (Fullston et al.,1999). In the case of rhenium sulphide, rhenium oxide formed due to oxidation is characterized by acidic properties $pH_{iep} = 4.22$ (Luxton et al., 2011). Thus stronger dependence of zeta potential on the electrolyte concentration, as in the case of many oxides, was observed for synthetic rhenium sulphide. As in the case of synthetic sulphide, sulphate groups were found which can form surface complexes with rhenium hydroxyl groups and in which sulphate ion can be exchanged into chloride ion of the background electrolyte. Thus, synthetic rhenium sulphide can exhibit dependence on pH and electrolyte concentration.

Conclusions

Synthesis of rhenium sulphide through the reaction of potassium perrhenate with sodium thiosulphate in the acidic medium leads to the preparation of the rhenium sulphide and sulphur mixture. In order to obtain pure sulphide it is necessary to remove sulphur by its dissolution in ether. To obtain rhenium sulphide in the form of dispersion of the grain sizes 0.5–4 μm it requires dispersion stabilization using Povidone K-25. The extrapolated pHiep value of synthetic rhenium sulphide is 2.3 for 0.001 mol/dm^3 NaCl. As for the commercial sample the extrapolated value pHiep is lower than 2. The synthetic sample exhibits stronger dependence of the zeta potential on the background electrolyte concentration than the commercial one due to surface oxidation during synthesis and/or purification.

References

COLEMAN K.S., SLOAN J., HANSON N.A., BROWN G., CLANCY G.P., TERRONES M., TERRONES H., GREEN M.L.H., 2002, *The Formation of ReS$_2$ Inorganic Fullerene-like Structures Containing Re4 Parallelogram Units and Metal-Metal Bonds,* J. Am. Chem. Soc., 124, 11580-11581.

DE LOS REYES J. A., 2007*, Ruthenium sulphide supported on alumina as hydrotreating catalyst*, Appl. Catal. A. 322, 106–112.

ESCALONA N., VRINAT M., LAURENTI D., GIL F.J., 2007 *Llambı´as, Rhenium sulphide in hydrotreating*, Appl. Catal. A. 322, 113–120.

FULLSTON D., FORNASIERO D., RALSTON J., 1999, *Zeta potential study of the oxidation of copper sulphide minerals*: Colloids and Surfaces A: Physicochem. Eng. Aspects 146, 113–121.

GÄRD R., SUN Z., FORSLING W., 1995, *FT-IR and FT-Raman Studies of Colloidal ZnS: 1. Acidic and Alkaline Sites at the ZnS/Water Interface*, J. Colloid Interface Sci., 169, 393–399.

HERLINGER' A.W., LONG T.V., 1969, *An Investigation of the Structure of the Disulfite Ion in Aqueous Solution Using Raman and Infrared Spectroscopies*, Inorg. Chem., 8, 2661−2665.

HIBBLE S. J., WALTON R.I., 1996, *X-Ray absorption studies of amorphous Re$_2$S$_7$.* Chem. Commun., 169, 393–399.

JUNFENG, Y. DUANZHI, M. XIAOFENG, G. ZILI, Z. JIONG, W. YONGXIAN, F.F. KNAPP JR., 1999, *[^{188}Re] Rhenium Sulphide Suspension: A Potential Radiopharmaceutical for Tumor Treatment Following Intra-Tumor Injection*, Nucl. Med. Biol., 26, 573–579.

KLETT R., LANGE U., HAAS H., VOTH M., PINKERT J., 2007, *Radiosynoviorthesis of medium-sized joints with rhenium-186-sulphide colloid: a review of the literature*, Rheumatology; 46(10), 1531–1537.

LUO J., ALEXANDER B., WAGNER T.R., MAGGARD P.A., 2004, *Synthesis and Characterization of ReO4-Containing Microporous and Open Framework Structures*, Inorg. Chem., 43, 5537–5542.

LUXTON T.P., EICK M.J., SCHECKEL K.G., 2011, *Characterization and dissolution properties of ruthenium oxides*, J. Colloid Interface Sci., 359, 30–39.

MURRAY H.H., KELTY S.P., CHIANELLI R.R., 1994, *Structure of Rhenium Disulphide*, Inorg. Chem., 33, 4418–4420.

PEAK D., FORD R.G., SPARKS D.L., 1999, *An in Situ ATR-FTIR Investigation of Sulfate Bonding Mechanisms on Goethite*, J. Colloid Interface Sci. 218, 289–299.

RÖNNGREN L., SJÖBERG S., SUN Z., FORSLING W., SCHINDLER P.W., 1991, *Surface reactions in aqueous metal sulphide systems: 2. Ion exchange and acid/base reactions at the ZnS single bond* H_2O *interface*. J. Colloid Interface Sci., 145, 396–404.

SCHWARZ D.E., FRENKEL A.I., NUZZO R.G., RAUCHFUSS T.B., VAIRAVAMURTHY A., 2004, *Electrosynthesis of* ReS_4*. XAS Analysis of* ReS_2*,* Re_2S_7*, and* ReS_4. Chem. Mater., 16, 151–158.

STARTSEV A.N., RODIN V.N., ZAIKOVSKII V.I., KALINKIN A.V., KRIVENTSOV V.V., KOCHUBEI D.I., 1996, *Silica-supported Sulphide Catalysts: IX. Synthesis and Properties of Structural Analogs of the Active Component of Hydrodesulphurization Catalysts.* Kinet. Catal., 38 (4) 548–555.

STELZER J.B., NITZSCHE R., CARO J., 2005, *Zeta Potential Measurement in Catalyst Preparations.* Chem. Eng. Technol., 28, 182–186.

TOWNSEND T.M., ALLANIC A., NOONAN C., SODEAU J.R., 2012, *Characterization of Sulphurous Acid, Sulfite, and Bisulfite Aerosol Systems*, J. Phys. Chem. A., 116, 4035–4046.

TU W., DENIZOT B., 2007, *Synthesis of small-sized rhenium sulphide colloidal nanoparticles,* J. Colloid Interface Sci., 310, 167–170.

ZHANG Q., XU Z., FINCH J.A., 1995, *Surface Ionization and Complexation at the Sphalerite/Water Interface: I. Computation of Electrical Double-Layer Properties of Sphalerite in a Simple Electrolyte,* J. Colloid Interface Sci., 169, 468–475.