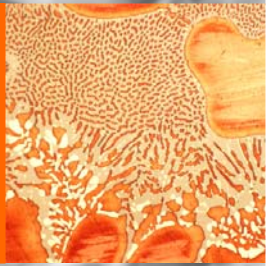
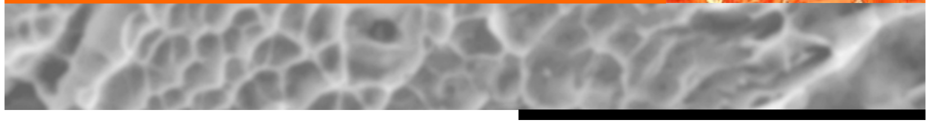
7th International Symposium on Technetium and Rhenium Science and Utilization
Moscow, 4-8 July, 2011
(ISTR-2011)

Method for hexamminecobalt(III) perrhenate synthesis from perrhenic acid





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Metali
Nieżelaznych

The goal of the work was to establish technology of pure anhydrous hexamminecobalt(III) perrhenate production from perrhenic acid solutions, obtained by ion exchange method, used in production of Re-Co powders

AMMONIUM PERRHENATE (APR) PRODUCTION IN POLAND

In Poland rhenium can be found in copper domestic concentrates at the level of 5 to 15 ppm

Mine	Rhenium content in the ore, g/Mg	Rhenium content in concentrate, g/Mg
ZG „Lubin”	1.22	8.2
ZG „Rudna”	1.41	12.1
ZG „Polkowice”	1.68	12.5

The concentrates are processed by KGHM Polska Miedz S.A. in three copper smelters:
Glogow I smelter,
Glogow II smelter,
Legnica smelter

The researchers of Institute of Non-Ferrous Metals (IMN) in Gliwice developed many technologies for recovery of rhenium from domestic resources, mainly in a form of ammonium perrhenate

In the result of cooperation between IMN and KGHM Ecoren S.A. two installations were constructed for recovery of rhenium, from week sulfuric acids, in a form of ammonium perrhenate of total capacity

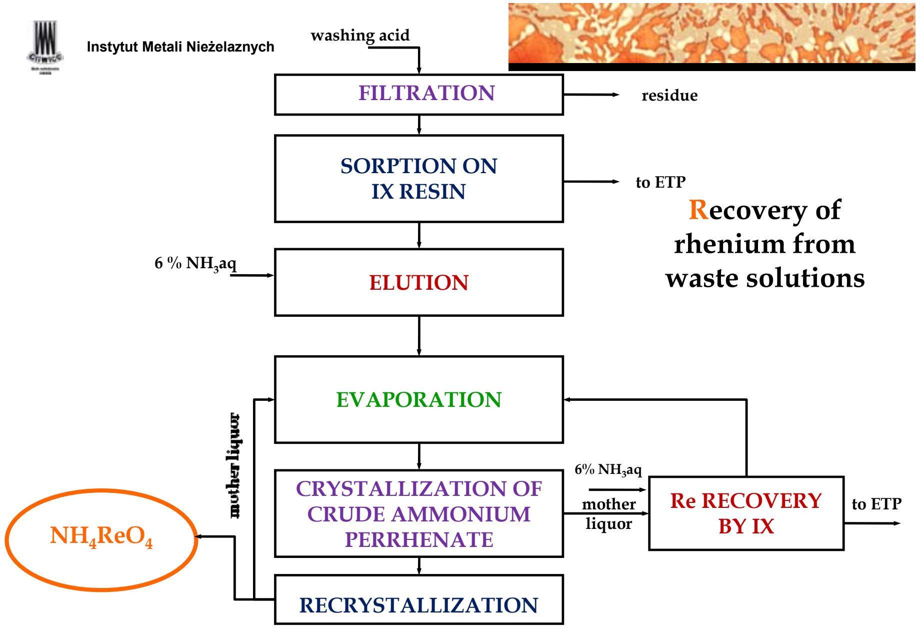
8 tons/year

The method was patented in Patent Office of the Republic of Poland in 2006

KGHM Ecoren is the single EU manufacturer of ammonium perrhenate produced from their own raw material

The acids contain on the average 20 mg/dm^3 of Re and many other impurities such as fluorine and arsenic compounds, as well as selenium, lead sulfate and chlorides

Recovery of rhenium from waste solutions



washing acid

FILTRATION

residue

SORPTION ON IX RESIN

to ETP

6 % NH_3aq

ELUTION

EVAPORATION

mother liquor

CRYSTALLIZATION OF CRUDE AMMONIUM PERRHENATE

6% NH_3aq

mother liquor

Re RECOVERY BY IX

to ETP

NH_4ReO_4

RECRYSTALLIZATION

The production of ammonium perrhenate from washing acids provided possibilities to undertake research on preparation of perrhenic acid directly from NH_4ReO_4

**Composition of NH_4ReO_4 (99.99 % purity): Re > 69.40 %,
Ca < 0.0005 %, K < 0.003 %, Mg < 0.0005 %,Cu < 0.0005 %, Na < 0.0005 %,
Mo < 0.0005%, Ni < 0.0005 %, Pb < 0.0005 %, Fe < 0.0005 %**

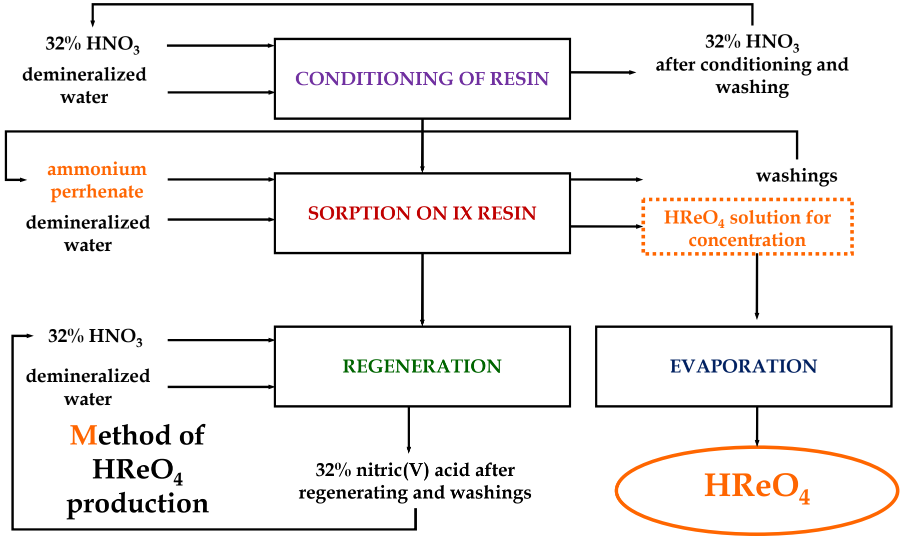
Synthesis od perrhenic acid

$$NH_4^+ReO_4^- + [\text{cation exchanger}]^-H^+$$

$$\downarrow$$

$$[\text{cation exchanger}]^-NH_4^+ + HReO_4$$

Method of $HReO_4$ production



32% HNO_3

demineralized water

CONDITIONING OF RESIN

32% HNO_3 after conditioning and washing

ammonium perrhenate

demineralized water

SORPTION ON IX RESIN

washings

$HReO_4$ solution for concentration

32% HNO_3

demineralized water

REGENERATION

EVAPORATION

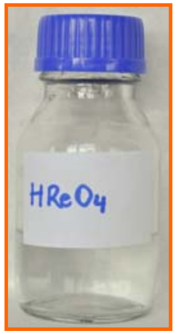
32% nitric(V) acid after regenerating and washings

$HReO_4$

Composition of $HReO_4$

300-900 g/L Re and

Ca < 0.001 %, K < 0.001 %, Mg < 0.0001 %, Cu < 0.0001 %,
Na < 0.0001 %, Mo < 0.0001 %, Ni < 0.0001 %, Pb < 0.0001 %,
Fe < 0.0001 %, 0.0003 % NH_4^+



The method was patented in Patent Office of the Republic of Poland in 2007

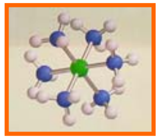
$[Co(NH_3)_6]Cl_3 + 3HReO_4 \longrightarrow [Co(NH_3)_6](ReO_4)_3 + 3HCl$

Cobalt compounds

commercial product $[Co(NH_3)_6]Cl_3$
by Acros Organics

hexamminecobalt(III) chloride
produced in laboratory

ammonia solutions containing cobalt

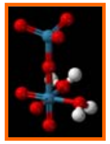


Rhenium compounds

perrhenic acid solutions

commercial product NH_4ReO_4
by KGHM Ecoren S.A.

anhydrous $Co(ReO_4)_2$
produced in laboratory



The following parameters were tested:

concentration of $[Co(NH_3)_6]Cl_3$

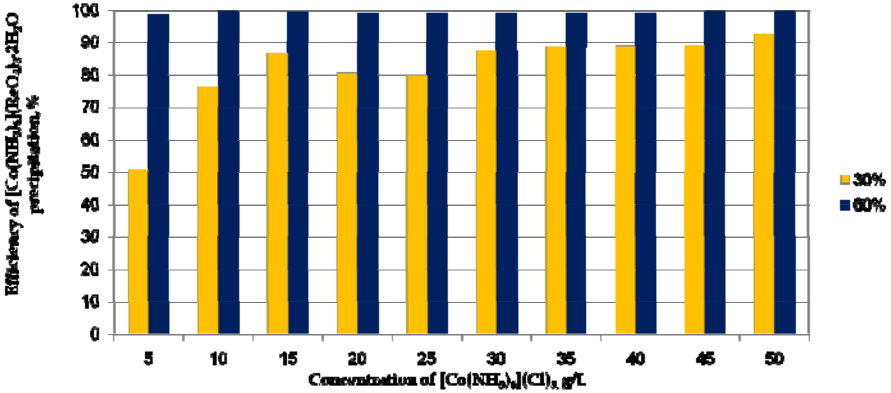
temperature

reaction time

excess of rhenium vs. cobalt

concentration of Re in $HReO_4$ solution

Concentration of $[Co(NH_3)_6]Cl_3$ influence on the efficiency of $[Co(NH_3)_6](ReO_4)_3 \cdot 2H_2O$ precipitation



Conditions: **concentration of $[Co(NH_3)_6]Cl_3$: 5.0- 50.0 g/L**, 670 g/L of rhenium content in $HReO_4$ solution, 30 and 60 % excess of rhenium vs. cobalt, temperature: 25°C, reaction time: ½ hour

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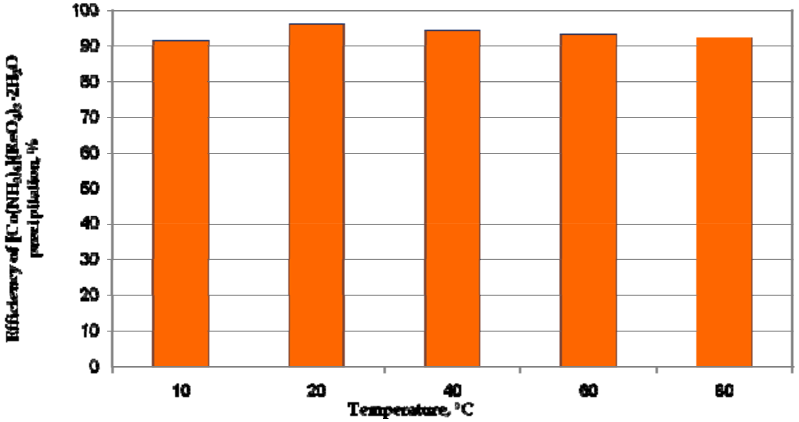
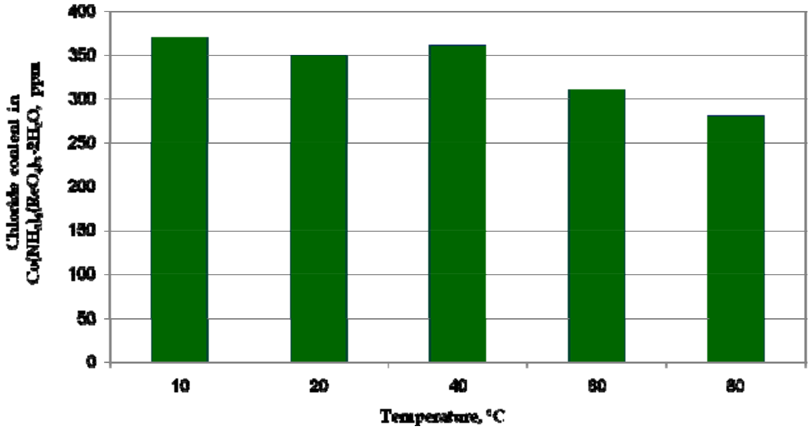
Temperature influence on the efficiency of $[Co(NH_3)_6](ReO_4)_3 \cdot 2H_2O$ precipitation



Conditions: **temperature: 10-80°C,** concentration of $[Co(NH_3)_6]Cl_3$: 30.0 g/L, 664 g/L of rhenium content in $HReO_4$ solution, 30 % excess of rhenium vs. cobalt, reaction time: ½ hour

Temperature influence on the chloride content in $[Co(NH_3)_6](ReO_4)_3 \cdot 2H_2O$



Conditions: **temperature: 10-80 °C,** concentration of $[Co(NH_3)_6]Cl_3$: 30.0 g/L, 664 g/L of rhenium content in $HReO_4$ solution, 30 % excess of rhenium vs. cobalt, reaction time: ½ hour

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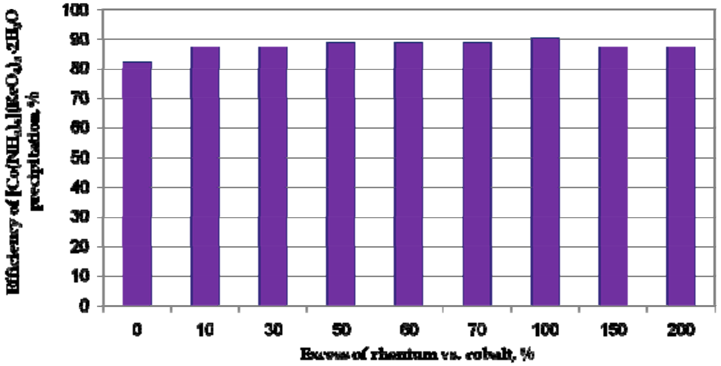
Reaction time influence on the efficiency of $[Co(NH_3)_6](ReO_4)_3 \cdot 2H_2O$ precipitation

Reaction time	Volume	Concentration of cobalt after precipitation	Mass of product	Composition of product			Efficiency
				Re	NH_3	Co	
h	mL	g/L	g	%			%
0.5	110	0.13	9.7	58.8	10.9	6.2	91.2
1	110	0.19	10.2	58.9	10.7	6.3	95.9
3	105	0.23	10.0	58.9	10.9	6.2	94.0
5	105	0.14	9.9	58.8	10.8	6.2	93.1

Conditions: **reaction time: ½-5 hours,** temperature: 25 °C, concentration of $[Co(NH_3)_6]Cl_3$: 30.0 g/L, 664 g/L of rhenium content in $HReO_4$ solution, 30 % excess of rhenium vs. cobalt

Excess rhenium vs. cobalt influence on the efficiency of $[Co(NH_3)_6](ReO_4)_3 \cdot 2H_2O$ precipitation



Conditions: **0-200 % excess of rhenium vs. cobalt,** reaction time: ½-hour, temperature: 25 °C, concentration of $[Co(NH_3)_6]Cl_3$: 20.0 g/L, $HReO_4$ contains 569 g/L Re

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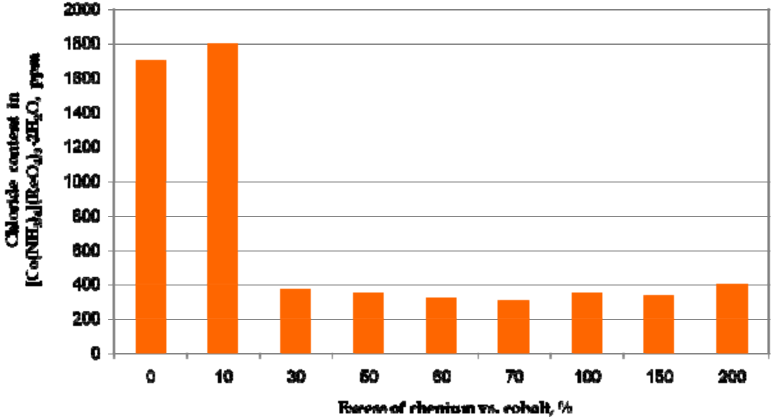
Excess of rhenium vs. cobalt influence on the chloride content in $[Co(NH_3)_6](ReO_4)_3 \cdot 2H_2O$



Conditions: **0-200 % excess of rhenium vs. cobalt,** reaction time: ½-hour, temperature: 25 °C, concentration of $[Co(NH_3)_6]Cl_3$: 20.0 g/L, 569 g/L of rhenium content in $HReO_4$ solution

Influence of rhenium concentration in $HReO_4$ on the efficiency of $[Co(NH_3)_6](ReO_4)_3 \cdot 2H_2O$ precipitation

Concentration of rhenium	Volume	Concentration in solution after precipitation		Composition of product				Efficiency
		g/L		Re	NH_3	Co	Cl	
g/L	mL	Co	Cl	%				%
508	108	0.0017	16.3	58.9	10.7	6.2	**1.00**	**99.3**
254	140	0.0016	13.4	58.9	10.6	6.1	**0.95**	**91.4**
127	168	0.0014	11.0	58.8	10.8	6.2	**0.90**	**89.1**
63	185	0.0014	9.6	58.7	10.9	6.2	**0.77**	**88.0**
31	223	0.0012	8.2	58.9	10.8	6.1	**0.68**	**73.3**
16	220	4.7	9.7	58.9	10.7	6.3	**0.08**	**49.1**

Conditions: **16-508 g/L of rhenium content in $HReO_4$ solution,** 60 % excess of rhenium vs. cobalt, reaction time: ½-hour, temperature: 25 °C, concentration of $[Co(NH_3)_6]Cl_3$: 50.0 g/L

Change of cobalt or rhenium source compouds

Rhenium compound	Cobalt compound	Composition of product			Efficiency
		Re	NH_3	Co	
		%			%
$HReO_4$	**commercial product $[Co(NH_3)_6]Cl_3$ by Acros Organics**	**58.9**	**10.7**	**6.2**	**90.3**
NH_4ReO_4		64.8	7.6	3.2	**-**
$Co(ReO_4)_2$		56.8	8.7	8.0	**-**
$HReO_4$	**commercial $[Co(NH_3)_6](ReO_4)_3$**	**58.8**	**10.7**	**6.2**	**90.2**
	$[Co(NH_3)_6](ReO_4)_3$ produced in laboratory	**58.9**	**10.7**	**6.2**	**92.3**
	cobalt containing ammonia solutions	**58.9**	**10.7**	**6.2**	**94.5**

Conditions: 60 % excess of rhenium vs. cobalt, reaction time: ½-hour, temperature: 25 °C

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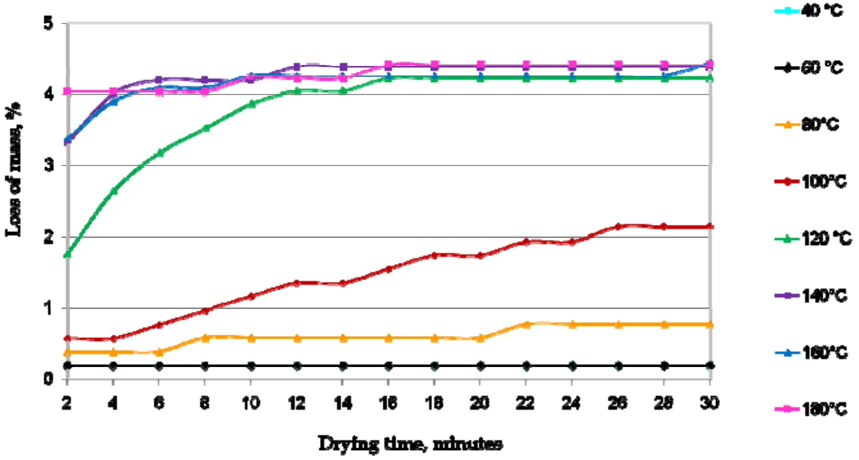
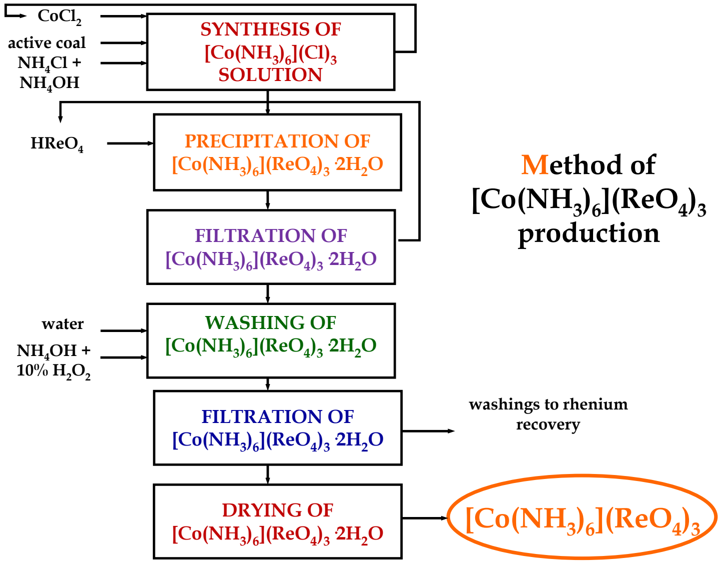
Thermal stability of $[Co(NH_3)_6](ReO_4)_3 \cdot 2H_2O$



Method of $[Co(NH_3)_6](ReO_4)_3$ production


$CoCl_2$

active coal

NH_4Cl + NH_4OH

SYNTHESIS OF $[Co(NH_3)_6](Cl)_3$ SOLUTION

$HReO_4$

PRECIPITATION OF $[Co(NH_3)_6](ReO_4)_3 \cdot 2H_2O$

FILTRATION OF $[Co(NH_3)_6](ReO_4)_3 \cdot 2H_2O$

water

NH_4OH + 10% H_2O_2

WASHING OF $[Co(NH_3)_6](ReO_4)_3 \cdot 2H_2O$

FILTRATION OF $[Co(NH_3)_6](ReO_4)_3 \cdot 2H_2O$

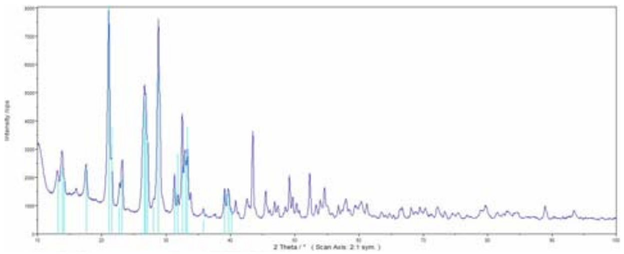
washings to rhenium recovery

DRYING OF $[Co(NH_3)_6](ReO_4)_3 \cdot 2H_2O$

$[Co(NH_3)_6](ReO_4)_3$

Composition of **$[Co(NH_3)_6](ReO_4)_3$**
61.2 % Re, 6.5 % Co, 11.2 % ammonium ions and
< 0.002 % chlorine, < 0.0005 % Na, Ca, Mg, Pb, Fe, Mo, Cr i Ni,
< 0.001 % K and < 0.0003 % Zn

The method was registered in Patent Office of the Republic of Poland in 2011



Conclusions I

It was found out that precipitation of $[Co(NH_3)_6](ReO_4)_3 \cdot 2H_2O$ should be conducted from solution of Co content at the level of 20-50 g/L, in room temperature, with 60 % excess of rhenium vs. cobalt

It is important to use aqueous solution of perrhenic acid where rhenium concentration is over 100 g/L

The combined solutions should be intensively mixed for half an hour so the cobalt concentration in the solution after precipitation of $[Co(NH_3)_6](ReO_4)_3 \cdot 2H_2O$ is <0.002 g/L

In the temperature level of 120 °C a stable anhydrous hexamminecobalt(III) perrhenate was formed

Conclusions II

The researchers of Institute of Non-Ferrous Metals in Gliwice developed many technologies for recovery of rhenium from domestic resources, mainly in a form of ammonium perrhenate and that material was then used for development of other rhenium technologies, such as: production of metallic rhenium, synthesis of perrhenic acid, production of other perrhenates: silver(I), nickel(II), cobalt(II) and iron(III), hexaaminnecobalt(III) as well as organic rhenium catalysts

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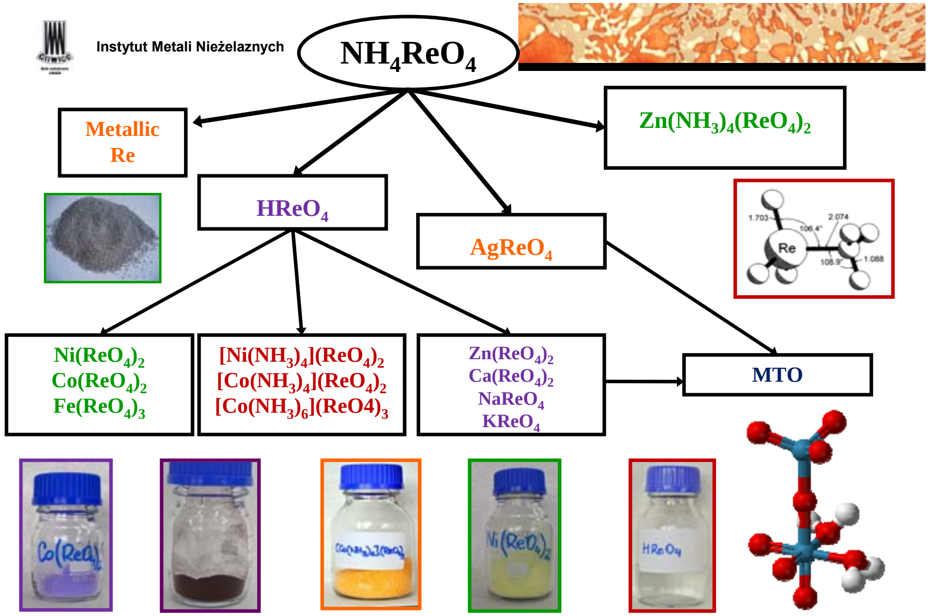

NH_4ReO_4

Metallic Re

$HReO_4$

$AgReO_4$

$Zn(NH_3)_4(ReO_4)_2$

$Ni(ReO_4)_2$
$Co(ReO_4)_2$
$Fe(ReO_4)_3$

$[Ni(NH_3)_4](ReO_4)_2$
$[Co(NH_3)_4](ReO_4)_2$
$[Co(NH_3)_6](ReO4)_3$

$Zn(ReO_4)_2$
$Ca(ReO_4)_2$
$NaReO_4$
$KReO_4$

MTO

History

- Established in 1952
- 1953 –launching of IMN Experimental Production Plant; currently Metal Processing Plant Inmet
- 1959 – incorporation of Light Metals Division in Skawina
- 1974 – establishment of Legnica Division
- 2007 – incorporation of Central Laboratory of Batteries and Cells

AB 073

Today

- Leading scientific centre of Polish non-ferrous industry
- One of the largest scientific institutes in Poland
- Over 500 employees
- Turnover above 100 million PLN
- R&D investment return index
- Certified laboratories

DET NORSKE VERITAS
MANAGEMENT SYSTEM CERTIFICATE

Instytut Metali Nieżelaznych

Research activities

- Mineral resources treatment and waste utilisation
- Non-ferrous metals metallurgy
- Hydrometallurgy
- Environmental protection
- Processing of metals and alloys
- Material science of metals
- Electrochemical power resources
- Analytical chemistry

Rok założenia
1952

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