# Lecture 10 Hydrometallurgy. Part 2

# *Processing of aqueous solutions*

Among the basic methods of aqueous solutions processing are:

1. Crystallization
2. Adsorption
3. Separation of compounds with low dissolubilities
4. Separation of metals using another metal – cementation
5. Separation of metals from solutions by gasses To an individual group belong:
6. Ion exchange
7. Fluid extraction

## Crystallization

In hydrometallurgy of NFMs, this process is used to separate metals in the forms of pure salts, to separate elements with similar properties by the method of repeated crystallization of salts, for solutions cleaning etc. Crystallization occurs during cooling of a saturated solution or during evaporation of a dissolving agent. The process can be divided into several steps:

* + - 1. formation of an oversaturated solution
			2. formation of crystallization nuclei – centers
			3. crystals growth
			4. re-crystallization

## Adsorption

The adsorption process includes two stages:

1. adsorption
2. separation of metals from adsorbents (desorption)

Some compounds have the ability to attach gases or liquids on their surfaces. This phenomenon is called sorption. Since sorption depends especially on the size of the sorbent’s surface, it is greater for porous or finely dispersed substances. For example charcoal, fine-grained oxides and hydroxides and colloidal substances are used in practice.

At present, adsorption is used to produce platinum, palladium and osmium from diluted chloride solutions on activated carbon, rhenium and molybdenum selectively from acid solutions, gold and silver from cyanide solutions and more. Cleaning of leachates from arsenic and antimony or from colloidal sulphur before electrolysis is based on the sorption ability of a freshly agglutinated Al(OH)3.

## Separation of metals from solutions using another metal – cementation

Coagulation of copper from mine waters using iron is one of the oldest hydrometallurgical processes. The basis of the process lies in displacement of a more noble metal from a solution of its salts by a less noble metal, which dissolves during the process. Dissolution of the less noble metal and coagulation of the nobler one occur due to different values of osmotic and dissolving pressures. During the process the dissolved metal charges negatively, while the surrounding solution charges positively.

The purity of a cemented metal is also influenced by contents of noble metals with which it coagulates. Therefore selective cementation is sometimes applied, during which the noblest metals are at first coagulated by a previously calculated addition of the cementing metal and subsequently, after their separation, the less noble metals are coagulated. This process is usual e.g. for cleaning of a zinc leachate from copper and cadmium. By application of a Zn powder, copper and subsequently cadmium coagulates are produced. To balance different concentrations of solutions, diffusion can be accelerated by increased temperature, flow of air bubbles or aqueous vapor.

## Separation of metals from solutions by gasses

Separation of metals from solutions by gasses processes at high temperatures and pressures,

while:

* + - 1. With increasing temperature, dissolubility of most of the salts in water increases up to 120 – 150°C and then decreases with further temperature increase.
			2. Dissolubility of salts in water usually depends on the presence of other salts. For example, dissolubility of CoSO4 in water at ambient temperature decreases strongly with a presence of (NH4)2SO4. At high temperatures, this dependence is opposite.
			3. Dissolubility of gasses in water decreases with increasing temperature up to approximately 100°C, while with further increase in temperature it increases remarkably.
			4. With a presence of salts, dissolubility of gasses usually decreases.
			5. At high temperatures, hydrolysis occurs easily.

### Reduction by hydrogen

Reaction of metal cations:

### Men+ + n/2 H2  Meo + nH+

can occur as long as the hydrogen potential is lower than the electrode potential of metal: **H2 < **Me. Separation stops after establishment of equilibrium.

### Reduction by carbon monoxide

Separation of silver and copper from sulphuric acid environment is possible via reduction by CO.

2 Ag+ +CO + H2O = 2 Ag + CO2 + 2 H+

Cu+ + CO + H2O  Cu + CO2 + 2 H+

Reducing ability of CO depends on the change of Gibbs molar energy of the reaction:

CO + H2O  CO2 + 2 H+ + e

The probable mechanism of reduction by CO can be described by the following equations (analogically for copper):

Ag+ + CO  Ag(CO)+ Ag(CO)+ + Ag+  Ag2(CO)2+

Ag2(CO)2+ + H2O  2 Ag + CO2 + 2 H+

### Separation by sulphur dioxide

Separation of copper sulphite from H2SO4 environment at ambient temperature is possible via reduction by sulphur dioxide. Nevertheless, if the process proceeds at 100°C and the pressure of 0.34 MPa, metal copper is separated.

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## Ion exchange

SO2 + H2O  H+ + HSO -

Cu2+ + HSO - + H O  Cu + HSO - + 2 H+

3 2 4

The ion exchange process is based on the ability of some substances to adsorb ions from a solution and to release ions with the same charge back to the solution (Fig. 3.11). These substances are called ion exchangers. Ion exchangers (ionexes) are dissoluble high molecular solid compounds containing active groups able to exchange ions for ions of dissolved electrolytes. According to the type of the exchanged electrons, they are denoted as catexes (cations) and anexes (anions). In hydrometallurgy, ionexes are applied especially for sorption of metals from highly diluted solutions, such as mine waters, waste waters from productions and leachates with low metals contents, further for sorption from mashes, for separation of chemically similar metals etc.



**Fig. 1** Principle of ion exchange [12].

Catexes usually substitute their hydrogen cations for an equivalent amount of other cations present in the liquid phase. A typical reaction of cations exchange is:

HR + NaCl  NaR + HCl where R denotes the catex body, which is actually a macro-anion.

According to their origin and principle, ion exchangers can be divided into the following groups:

* + - 1. mineral ion exchangers – inorganic
			2. organic ion exchangers

There are natural and fabricated ion exchangers in both the groups. Among natural inorganic catexes are aluminosilicates belonging to the mineralogical groups of hydrated micas, montmorillonites or zeolites. Comparing to synthetic catexes they have relatively low capacities. The general formula of zeolite is:

MeO.Al2O3.nSiO2.mH2O

where Me can be Li, Na, K, Ca, Ba.

## Solvent extraction

Extraction is a process of conversion of compounds from aqueous solutions to liquid organic phases non-miscible with water (Fig. 3.12). Subsequent re-extraction enables conversion of an extracted metal from the organic phase to an aqueous solution. The organic phase returns back to the process.

Extraction is, similarly to ion exchange, applied in hydrometallurgy to produce metals form diluted solutions and enables their separation from various admixtures. At present, extraction is applied to clean uranium, indium, thallium, germanium, tellurium, to produce copper and separate nickel, cobalt, hafnium, molybdenum and rhenium.

Extrahents are organic compounds forming complexes or salts with the extracted metals, which dissolve in the organic phase. They are organic acids, alcohols, ethers, ketones, amines and others. Dissolvents are organic liquids non-miscible with water dissolving the extrahents. The usually applied dissolvents are kerosene and its fractions.

Extraction processes can be divided into:

* + - 1. extraction based on cations exchange,
			2. extraction based on anions exchange,
			3. extraction by neutral extraction agents after prior solvation or hydrosolvation.



**Fig. 2** Principle of solvent extraction [13].

1. What is the principle and application of in-situ leaching?
2. What are the mothods used for solid-liquid separation?
3. Which factors do influence the selection of leachning reagents?
4. How can the ion exchangers be divided?