PROCESSING OF LIQUID INDUSTRIAL WASTE FROM THE POTASSIUM PRODUCTION

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In Ukraine, in particular in Prikarpattya region unique polymineral ores are located. Over 10 different minerals are included in their composition (actually that is why they are polymineral). Especially intensive development of polymineral ores was conducted in the days of the USSR. Then from nature only took and took more valuable components on this moment. For example, from polymineral ores of Prikarpattya only partly withdrew potassium salts and magnesium, and all of other was thrown out, forming the dumps of saliferous wastes, landfills, – enormous «dead» lakes (fig.1), which not only occupy considerable amounts of lands which are withdrawn from the agricultural use but also create a permanent threat for nature and adjoining settlements.

Figure 1. “Dead” lakes (Stebnyk sludge pits)

The idea is not only that other components of these ores were unnecessary. Simply not able to separate them, because not only then – to today's time the theory of physical and chemical processes in the multicomponent water-salt systems did not attain a necessity for this level. Laboratory researches were and remain very labour intensive and can not give enough information, necessary for a theoretical

analysis and engineerings calculations, but consequently and planning of productions for the complex wasteless redoing of polymineral ores.

There are two basic methods of polymineral ores redoing. First, galurgic, based on selective dissolution and crystallization of salt components of ore. The second one – flotation, needs less energy, but it's wastes require the large landed areas for building of landfills, harmful influence on an environment and remain the serious threat of ecocatastrophes.

Exploitation of potassium mineries lasted in Stebnyk and Kalush resulted in formation under earth and accumulation on surface (as a result of annual pumping from mines into landfills) over 13 million m^3 brines which contains such elements as K, Na, Mg, S, Cl, Ca, and also a lot of oligoelementss. This undesirable and almost out of control process resulted in formation of large supplies of raw material from which it is possible to get valuable products.

In times of exploitation of "Polymineral" accumulated more than 25,5 millions tone of wastes (in thereby 4,2 millions tone of liquid phase). Wastes are the proof enough micronized suspensoidss. They accumulate and saved practically without limitation of term in landfills, which became the permanent threat of ecocatastrophes. The most happened on Stebnyk's landfill in 1983. For short time of r. Dnestr 4,5 million m^3 brines were outpoured, content of salts in which arrived at 335 g/l; river water on great while became useless for all of water users.

Landfill constantly contaminates the Tismenicya and Dnistr rivers, surplus of which, over 1 million m^3/year, appears as a result of exceeding of volume of fallouts above evaporation. There are proximate economic damages: on a supervision and maintenance of landfill annually lost near 1 million UAH

For today in the district of Stebnyk appeared near 33 million m^3 of underground cavities. As a result of destruction of supersalt breeds as a result of dissolution from atmospheric fallouts and ground-water there are changes of earthly surface, failures and karstic watering-cans appear. During the last ten years intensively broaden and deepen failures are before formed on territory of Stebnyk mine №2. On a prognosis, present 670 m^3 of karstic cavities pressed for six years increased on 217 thousands of m^3.

However that's not only in geochemical and geological processes which take a place in natural terms. Ten of millions of cubic meters of ore – from the third to the half of all of extraction – was not used for the receipt of products, and as wastes became the source of permanent ecological threat. Wastes differ from ore only less content to potassium and magnesium, by the greater particle of gypsum, mirabilit and insoluble remain. On condition of the use of wasteless technologies from wastes and ore it is possible to get identical products, though in other correlations:

Average salt composition of polymineral ores and wastes, the masses.%

	$MgSO_4$	$CaSO_4$	Na_2SO_4	KCl	K_2SO_4	NaCl	H.З.	H_2O
Ore	23	4	-	11	5,1	34	14	8
"waste"	0,6-4,3	7,5-13,2	4,9-12,1	4,0-8,7	-	4,8-28,2	25-58	3,4-17

As a result of dilution and next dissolution of hard phase fallouts composition of brines changes, and for planning of rational technology of their redoing it's necessary to make a complex estimation. Without regard to possibilities of flexible technologies, the best results are arrived if a technological process operates in the stationary mode which provides stabilizing of sizes of streams and their composition.

Therefore there will be expedient averages will make brines which will be selected for processing from the different points of landfill and mineries. Determining in this process is correlation of salt ingridients of liquid phase. Especially interesting is a fact of practically functional linear connection of sum of ions ($2K+Mg+Cl_2$) and ($2Na+SO_4$). This dependence allows to pull out a hypothesis about possibility of division these two groups of ions in the properly organized technological process.

Principles and methods of mathematical models of interphase equilibrium construction are developed for a variable temperature in the multicomponent water-salt systems (WSS) on the basis of quadratic forms.

The analytical presentation of equilibrium in unisothermal multicomponent WSS on the basis of modern theory of solutions rarely gives reliable results, that is why in the calculations of technological and nature protection processes, as a rule, graphic methods were used.

The method of mathematical models of interphase equilibrium construction is offered in multicomponent WSS on the basis of the idea that in each (n+1)-concentration space the great number of figurative points of solutions, which are in the equilibrium with a separate mineral, forms a hypersurface which at (n+1) = 2 grows into a line.

On the basis of information technologies methods and algorithms of mathematical design of polytermal interphase equilibrium in the multicomponent water-salt systems, in particular on the basis of translation principle, and also analysis and prognostication of trajectories of izohydric and polytermic processes of interphase transformations, as basis of wasteless technologies of polymineral ores water salt wastes processing creation are developed and approved. By the leadthrough of numerical experiments on the PC the wasteless technology of sylvinit ores division, utilization of salt components of sewer water of soda production and wasteless conversion in the mutual quarternary system was developed.

From two methods of processing of polymineral ores – flotational and galurgical, second separately, or in combination with the first, can become a basis of wasteless production, and also utilizations of the accumulated wastes. Mathematical model, which has been developed, engulfs the design of terms of interphase equilibrium and trajectory of processes of interphase transformations are scientific basis of such processes.

On the basis of translation principle the algorithm of alternative method of construction of mathematical models of interphase equilibrium is developed in multicomponent WSS, when it is not enough empiric information about an equilibrium.

Developed and approved mathematical model and algorithms of prognostication of trajectories of near-equilibrium processes of interphase transformations in multicomponent WSS, as bases of the automated planning of ecologically effective productions and utilization of salt wastes. A mathematical model designe the wasteless technological processes. They can be examined as combination of the izohydric heating-cooling processes, isothermal evaporation or addition of water in the system from outside, crystallization of minerals, dissolutions of hard phases. Combination of simple processes is basis of optimum technologies organization according to the ecological and economical criteria.

Figurative point of solution, equilibrium with any mineral of this WSS, is determined as crossing of one ray of simple processes with the surface of equilibrium solutions.

Mathematical models and algorithms of calculation of trajectories of processes in WSS consist of a few typical blocks, which are involved from the main programmatic module depending on the set sequence of operations in the chosen technological process.

1st stage: evaporation of solution, unsaturated in relation to all of minerals of the system to the moment of satiation by one of the minerals.
2-nd stage: evaporation with crystallization of one mineral.
3-rd stage: compatible crystallization of two minerals.

Principles of construction of trajectory of wasteless processes of conversion are considered on the example of the quarternary system $NaNO_3$+KCl = NaCl+KNO_3-H_2O, which has a practical value, in particular in the production of potassium nitrate by the method of conversion of KCl and $NaNO_3$. Possibility of wasteless technology is grounded from theoretical the hundred-per-cent output of KNO_3 in relation to both ingredients – KCl and $NaNO_3$, and at the same time – clean NaCl as the second, byproduct; determination in theory and optimum parameters are tested experimentally each of the stage of technological cycle: value of temperatures and concentrations of salt components in the solutions.

Also the optimum parameters of mirabilite freezing process from Stebnyk WSS are experimentally certain, and are fixed in basis of stand fluidizer production of waterless sodium sulfate from Stebnyk WSS project, as the first key stage of their utilization (temperature of the process -4 ÷ -5 °C).