On some features of low-temperature mixed crystallization of CsI solutions obtained from industrial wastes

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Investigation of multiple low-temperature mixed crystallization (LTMC) of the solution wastes of cesium iodide was reported. LTMC is a very simple and convenient way for an essential decrease of the concentrations of practically all the admixtures including isomorphic ones (Na, K, Rb). However, LTMC results in CsI enriching with Tl, which enters into the crystallized fraction. Due to the presence of considerable amounts of Na and sulfate admixtures during the first 3–4 LTMC the displacement of other admixtures occurs with lower intensity comparing with the following LTMC stages and the threshold concentration of Na is ca. $5 \cdot 10^{-2}$ wt.%. For Na the effective purification coefficient β is 0.6–0.7 for the initial solution and it reduces to 0.35–0.5 in more pure solutions, for K these values are 0.75 and 0.5–0.55. Na content does not affect Rb distribution and for this admixture $\beta \approx 0.65–0.75$ for all the solutions. For Cu the value of β is close to 1 since CuI is insoluble in water and LTMC favors its entering in the solid fraction. β value for Tl admixture is ca. 1.06 that means the enriching of the final product of LTMC with respect to this admixture. The removal of sulfates from CsI using LTMC occurs very easy.

Keywords: cesium iodide, wastes, low-temperature mixed crystallization, effective purification coefficient.

Проведено изучение многократной низкотемпературной смешанной кристаллизации (НСК) техногенных растворов йодида цезия. Этот метод является простым и удобным для существенного снижения концентрации практически всех примесей, в том числе изоморфных (Na, K, Rb). Однако в процессе кристаллизации продукт обогащается примесью таллия, который преимущественно входит в закристаллизовавшуюся часть. Вследствие значительного загрязнения техногенных отходов примесями натрия и сульфатов в течение первых 3–4 НСК процесс вытеснения других примесей происходит менее интенсивно,чем впоследствии, пороговая концентрация ионов натрия — $5 \cdot 10^{-2}$ wt. %. Для натрия эффективный коэффициент очистки β находится в пределах 0,6–0,7 для исходного раствора и по мере очистки уменьшается до 0,35–0,5, для калия соответствующие значения 0,75 и 0,5–0,55, для рубидия – $\beta = 0,65–0,75$ и не зависит от содержания натрия. Для меди эффективный коэффициент очистки близок к единице вследствие того, что CuI нераство-

рим в воде и при кристаллизации преимущественно входит в закристаллизовавшуюся часть. Для таллия эффективный коэффициент очистки несколько больше единицы, что указывает на последовательное накопления этой примеси в продукте при НСК. Сульфат-ионы достаточно легко вытесняются в процессе НСК отходов производства монокристаллов йодида цезия.

Особливості низькотемпературної мішаної кристалізації розчинів йодиду цезію, одержаних з промислових відходів. *А.Ю.Бояринцев, В.Л.Чергинець, Т.В.Пономаренко, Т.П.Реброва, А.Г.Варич, К.Ю.Брильова, О.М.Карякіна, Т.В.Шеїна, В.В.Варченко, О.І.Юрченко.*

Багаторазова низькотемпературна мішана кристалізація (НМК) техногенних розчинів йодиду цезію є простим і зручним методом для суттєвого зниження концентрації практично усіх домішок, у тому числі ізоморфних (Na, K, Rb). Однак у процесі кристалізації продукт збагачується домішкою талію, який переважно входить у закристалізовану частину. Внаслідок значного забруднення техногенних відходів домішками натрію і сульфатів протягом перших 3–4 НМК процес витіснення інших домішок відбувається менш інтенсивно, ніж надалі, порогова концентрації іонів натрію — $5 \cdot 10^{-2}$ мас.%. Для натрію ефективний коефіцієнт очищення, β, знаходиться у межах 0,6–0,7 для вихідного розчину і в міру очищення зменшується до 0,35–0,5, для калію відповідні значення 0,75 і 0,5–0,55, для рубідію $\beta = 0,65$–0,75 і не залежить від вмісту натрію. Для купруму ефективний коефіцієнт очищення близький до одиниці внаслідок того, що CuI є нерозчинним у воді і при кристалізації переважно входить у закристалізовану частину. Для талію ефективний коефіцієнт очистки є трохи більшим від одиниці, що вказує на поступове накопичення цієї домішки у продукті при НМК. Сульфат-іони досить легко витісняються у процесі НМК відходів виробництва монокристалів йодиду цезію.

1. Introduction

Single crystals based on alkali metal iodides (mainly, CsI and NaI) are widely used for the creation of working parts of optical equipment of different applications. In particular, CsI crystals are applied for making windows transparent in IR range due to their low hygroscopicity and the absence of absorption bands in the said part of spectrum [1]. The main part of the iodide single crystals (CsI, CsI:Na, CsI:Tl, NaI:Tl) is scintillation detectors applied for different purposes (medical tomography, high-energy physics, cosmic and nuclear instrument engineering, the logging of drill holes etc.) as detectors of the ionizing radiation of various origin [2]. Annual production volume of the scintillation single crystals is several dozens of tons.

The said single crystals are grown, mainly, by Chokhralski or Kyropoulos methods that permits to grow crystals with masses of several hundred kilos within short interval of time. For the practical applications the grown cylindrical crystals are cut to smaller parts of various geometry. Besides, some pieces with inclusions, cracks, turbidities and other visual defects are removed. Thus, an appreciable part of the grown crystal passes into wastes: nonused solidified melt and deposit from the walls of the growth apparatus, rest pieces (cuttings) which are dissolved in water for the waste unification. These wastes are a serious problem for crystal manufactures and this problem requires urgent solution. The best solution of the waste problem is the returning of the valuable constituents of these wastes (iodine, cesium and thallium) in the production. The separation of thallium does not present a serious problem since TlI is practically insoluble in water and slightly soluble in iodide solutions. In the latter case the dependence of the solubility against alkaline metal iodide concentration passes through the minimum corresponding to mass fraction of iodide in the solution within 10–15 wt. %. The following treatment of NaI wastes is very simple since the solution after TlI separation contains only one valuable components — iodine. So, the waste solution is acidified and hydrogen peroxide is added to complete precipitation of I_2 which is separated from solution by filtration and further it is purified by sublimation.

The processing of CsI wastes is more complicate since they also contain cesium besides iodine. Due to this reason the solution after TlI separation is treated by $Ba(OH)_2$ to precipitate sulfates (as $BaSO_4$) and heavy metals, aluminum and magnesium (insoluble hydroxides). Further this solution is treated by Cs_2CO_3 to precipitate the excess of barium, alkaline earth metals (as carbonates). Nevertheless, such a way of

purification does not provide the separation of alkali metal cations (residual content of sodium is varied from 0.1 to 1 wt. %). The removal of alkali metal cations is the hardest problem, which is solved by multiple recrystallization from aqueous solutions. The above-described method possesses essential disadvantage caused by relatively small changes of CsI solubility with the temperature: from 80 g/100 g of water at 20°C to 200 g/100 g of water at 100°C [3, 4]. It is obvious that one cycle of recrystallization leads to the loss of approximately 40 % of CsI in the mother waters and the direct yield of CsI after 3rd recrystallization is ca. 25 %. The treatment of the mother waters is difficult since the concentration of admixtures in them is considerably higher than in the initial solution. This forces engineers to consider alternative approaches of crystallization or chemical treatment of the waste solutions, which can result in higher yield of extra pure CsI free from Na, K and Rb.

Studies of the low-temperature direct crystallization (LTDC) of water-salt eutectic mixtures (WSE) are originated from analytical methods of determination of admixture concentration in the cases where their content is lower than the detection limit. Thorough consideration of the LTDC was performed in the monograph by A.B.Blank [5] where the distribution coefficient for main admixtures at CsI–H_2O WSE crystallization were presented. The problem of deep purification of CsI using LTDC was solved in [6]. For this purpose authors took extra pure CsI with the total concentration of admixtures ca. 10^{-3} wt. % . The purification resulted in the decreasing of the concentrations of heavy and transition metals to level lower than 10^{-5}–10^{-6} wt. %. Concentrations of alkali metals also reduced although the corresponding quantitative data were absent.

So, there are certain preconditions for the use of LTDC for the purification of technogenic solutions of cesium iodide, although the above-mentioned results cannot be used immediately since the level of admixtures in the salts used in [5, 6] was lower by 2 orders of magnitude than usual level of the wastes contamination. Ditto, the complicated equipment was used there for LTDC:tank with antifreeze (for cooling to −17°C), system for antifreeze stirring, system for rotation of vessel (10 l) with the water-salt eutectic. Considerable volumes of WSE favored the slowing of the crystallization process due to the slight thermal

conductivity if the solid WSE. This forces the searching for a new design of LTDC under industrial conditions.

One of ways of developing this routine can be deduced from the fact that usual industrial mass crystallization finishes at room temperature (*rt*) and the remaining mother waters contain about of 40 wt. % of CsI whereas the corresponding concentration of CsI in WSE is only 27.5 wt.%. It is of interest to study the process of cooling the solution saturated at *rt* to crystallize some additional amount of CsI and, then, at -5.6 °C WSE. However, such investigations were not performed before. Since in this process crystallization of WSE follows usual mass crystallization (cooling from *rt* to WSE point) we called this crystallization routine low-temperatire mixed crystallization, LTMC. Its features are discussed below.

2. Experimental

Preparation of CsI solution. The technogenic CsI solution was thermostated and its density was measured ($\rho = 1.10$ g·cm^{-3}). This density corresponds to CsI concentration ca. 12 wt. % assuming that admixture amount in the solution can not appreciably affect its density. Then the solution was evaporated to CsI concentration near 38-40 wt. % that was controlled by the loss of the solution wt. Then the cooled solution was separated from the deposit of carbonates ($CaCO_3$, $MgCO_3$) and calcium sulfate and further it was used for LTMC.

LTMC. The process was performed in usual freezing chamber cooled to −12°C. 1.5 l PET bottles from mineral or potable water were used as containers. The crystallization degree was 0.96–0.97 and the time required for LTMC was ca. 36 h. After each LTMC cycle ca. 50 ml of residual solution was removed, the frozen WSE was heated to the formation of homogeneous solution which was subjected to following LTMC (up to 10 cycles). After each LTMC samples of the product and mother waters were evaporated, dried and analyzed.

It should be noted that the first 3 cycles of LTMC occurred without ordered crystallization from vessel walls inside that could be caused by spontaneous formation of crystallization centers into whole bulk caused by the admixtures. Beginning with 4th LTMC there was the directed movement of the crystallization front into the vessel and time necessary for the crystallization somewhat reduced.

Table 1. Concentrations of certain admixtures (in wt. %) in cesium iodide purified using multiple LTMC, $g = 0.96–0.97$

LTMC No	Concentration, wt.%					
	Na$^+$	K$^+$	Rb$^+$	Cu$^+$	Tl$^+$	SO$_4{}^{2-}$
Initial solution	0.29	0.0058	0.00013	0.000015	0.00020	>0.01
1	0.21	0.0045	0.0001	0.000057	0.000068	>0.01
2	0.13	0.0035	0.00008	0.000026	0.000065	>0.01
3	0.095	0.0019	0.00006	0.00002	0.000068	>0.01
4	0.053	0.00098	0.00004	0.000017	0.000083	0.008
5	0.028	0.0005	0.00002	0.000011	0.000087	0.002
6	0.011	0.00028	0.00002	0.000017	0.000084	0.001
7	0.0056	0.00018	<0.00002	0.000019	0.000083	<0.0005
8	0.002	0.00015	<0.00002	0.000017	0.00011	<0.0005
9	0.0014	0.00008	<0.00002	0.000016	0.00010	<0.0005
10	0.00044	0.00005	<0.00002	0.000008	0.00011	<0.0005

Table 2. Concentrations of certain admixtures (in wt. %) in cesium iodide from mother waters after multiple LTMC, $g = 0.96–0.97$

LTMC No	Concentration, wt.%					
	Na$^+$	K$^+$	Rb$^+$	Cu$^+$	Tl$^+$	SO$_4{}^{2-}$
Initial solution	0.29	0.0058	0.00013	0.000015	0.000015	0.29
1	0.62	0.027	0.0007	0.00018	0.000015	0.62
2	0.87	0.037	0.0012	0.00021	0.000015	0.87
3	0.43	0.02	0.0005	0.00014	0.000015	0.43
4	0.44	0.02	0.00055	0.00015	0.000015	0.44
5	0.21	0.01	0.0003	0.000082	0.000015	0.21
6	0.12	0.0056	0.00015	0.000057	0.000015	0.12
7	0.09	0.003	0.00009	0.000039	0.000015	0.09
8	0.075	0.0014	0.00005	0.000023	0.000015	0.075
9	0.025	0.00045	0.00003	0.000008	0.000015	0.025
10	0.0009	0.00033	0.00002	0.000011	0.000015	0.0009

Determination of thallium and copper in CsI was performed by differential pulse anodic stripping voltammetry after processing of samples with concentrated nitric acid. Voltammetric measurements were carried out at a hanging mercury drop electrode as a working electrode using 797 VA Computrace (Metrohm, Switzerland). An acetic buffer solution with EDTA (pH 5.5) was chosen as a supporting electrolyte. Peaks of thallium and copper were observed at −0.45 V and −0.23 V (versus Ag/AgCl (3 M KCl)), respectively. Flame spectrometry was used for Na, K, and Rb determination. Measurements were carried out using iCE 3500 atomic absorption spectrophotometer (Thermo Fisher) in an emission mode. Flame of acetylene-air gaseous mixture was used as an excitation source. The low determination limit for Na and K is $2 \cdot 10^{-5}$ and for Rb — $5 \cdot 10^{-6}$ wt. %. Relative standard deviation values for concentration interval of $2 \cdot 10^{-5}$ to $2 \cdot 10^{-1}$ wt. % are within the range of 0.01–0.15.

Reaction of barium sulfate formation was used for turbidimetric determination of sulfates. Solvent composition (water, 10 % ascorbic acid solution, precipitating agent: 5 % barium chloride solution, diethylene

glycol, ethanol (1:3:3 by volume)) and temperature regimen provide obtaining a stable suspension of desired dispersity. The low determination limit is $5 \cdot 10^{-4}$ wt. %. Determination error was not greater than 9 %.

3. Results and discussion

We considered the obtained results from the viewpoint of chemical engineering meaning that multiple LTMC is the cascade consisting of several separation elements (*se*). For the separation element "*i*" we have the following situation. The product from "*i*−1" stage with admixture concentration of y_{i-1} entered in se_i and the product from "*i*" stage with admixture concentration of y_i (lower than y_{i-1}) and mother waters with admixture concentration of x_i (higher than y_{i-1}) leave the se_i.

The operation efficiency of *se* is characterized by the purification coefficients. The thermodynamical purification coefficient α is calculated as:

$$\alpha = y_i / x_i, \qquad (1)$$

whereas the effective purification coefficient β is estimated as follows

$$\beta = y_i / y_{i-1}. \qquad (2)$$

The initial data used for the analysis of the purification efficiency are presented in Tables 1 (product) and 2 (mother waters), here the crystallization degree was in $g = 0.96-0.97$ range.

On the distribution of alkali metal admixtures at LTMC.

The difficulties arising at the purification of cesium iodide from alkali metal cations are caused by the fact that Na^+, K^+ and Rb^+ are isomorphic to Cs^+.

Na^+ admixture is referred to the most abundant (from CsI:Na and Cs:Tl which is doped also by Na^+) and harmful contaminations (it makes the salt hygroscopic). The dependences of Na^+ concentration in the crystallization product and mother waters and purification coefficients are presented in Fig. 1. The obtained dependences (at least, 1−3) can be conditionally split in two sections one of which corresponds to strongly polluted solutions (Na^+ concentration exceeds 0.1 wt. %) and other is referred to relatively pure ones. As is seen, at cycles 1−3 sodium concentration in the solution remains practically unchanged that demonstrates the features of strongly polluted CsI solutions comparing with the lit-
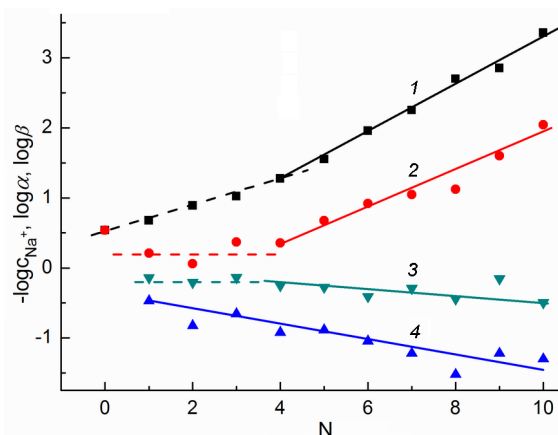

Fig. 1. The dependence of logarithm of Na concentration ($-\log c_{Na}$) in product (*1*), mother waters (*2*) and logarithms of thermodynamic (α) and effective (β) purification coefficients on numbers of LTMC cycles (*N*).

erature data for LTMC of solutions of extra pure CsI. The low efficiency of the purification can be caused by the fact that concentration of sulfate ions in the initial solution are also high and Na_2SO_4 is able to form cryohydrate ($T = 272$ K, concentration of Na_2SO_4 is ~4 wt. %, phases are $Na_2SO_4 \cdot 10H_2O$ and ice [7]).

As for the dependences of concentrations, they can be approximated by such lines:

$$-\log c_{Na} = a + N(-\log\beta), \qquad (3)$$

where a the free term. The initial section of the dependence 1 ($N \leq 3$) is approximated as follows:

$$-\log c\ (\pm 0.02) + 0.167(\pm 0.01) \cdot N,\ \beta = 0.68\ . \qquad (4)$$

Thus, the process of displacement of sodium into mother waters is more difficult at high admixture concentrations. However, the purification becomes more effective after the 3rd cycle and the corresponding dependence is as follows:

$$-\log c_{Na} = -0.04(\pm 0.07) + 0.332(\pm 0.01) \cdot N, \qquad (5)$$

here $\beta = 0.465$. As for α values, for initial cycles they exceed value of 0.1 obtained by Blank [5] and for conditionally pure solutions it agrees with the literature parameter. So, considerable contamination of cesium iodide wastes with sodium essentially complicates the purification process and it requires 3−4 additional LTMC cycles.
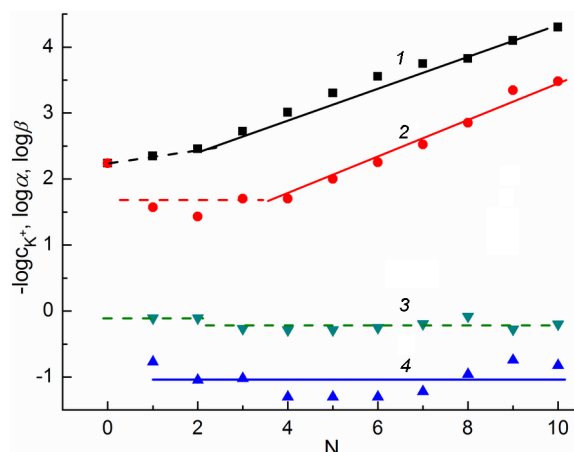
Fig. 2. The dependences of logarithm of K concentration ($-\log c_K$) in product (*1*), mother waters (*2*) and logarithms of thermodynamic (α) and effective (β) purification coefficients on numbers of LTMC cycles (*N*).
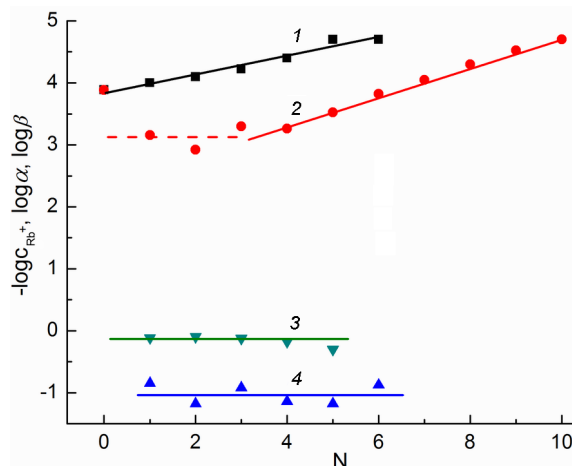

Fig. 3. The dependences of logarithm of Rb concentration ($-\log c_{Rb}$) in product (*1*), mother waters (*2*) and logarithms of thermodynamic (α) and effective (β) purification coefficients on numbers of LTMC cycles (*N*).

Let us consider results concerning potassium distribution at LTMC of the liquid wastes of CsI. This admixture is especially undesirable in CsI since natural potassium contains ^{40}K isotope (0.0117 %, β-, $\tau_{1/2} =$ 1.18·10^9 years [8]) causing appreciable intrinsic radiation background in the scintillators. The imagination about the behavior of K admixture during multiple LTMC of CsI solution can be obtained from Fig. 2.

The statistical treatment of the initial section ($N \leq 3$) yields the approximation:

$$-\log c_K = 2.237(\pm 0.001) + \quad (6)$$
$$+ \ 0.110(\pm 0.001) \cdot N, \quad \beta = 0.7.$$

At $N > 3$ the dependence is as follows:

$$-\log c_K = 2.08(\pm 0.07) + \quad (7)$$
$$+ \ 0.226(\pm 0.001) \cdot N, \quad \beta = 0.60.$$

That is, similarly to Na distribution, high common concentration of technogenic admixtures retards the purification of CsI the solution from potassium and this can be seen from β values. As for α values, although they oscillate near 0.1 ($\log \alpha = -1$, this value agrees with [5]) it is seen from dependence 1 that this parameter decreases with the increase of N and somewhat grows during the latest stages. This can be explained both by accuracy of analytical determination of K and the fact that at extremely low concentration of an isomorphic admixture its distribution coefficient (and, hence, α) grows since the amount of the admixture becomes comparable with the

quantity of defects arising in the solid fraction. In this case the admixture is captured by the defects.

Besides potassium, Rb is also referred to very undesirable admixtures in cesium iodide since the natural rubidium contains 28.75 % of ^{87}Rb (β-, $\tau_{1/2} = 4.8 \cdot 10^{10}$ years) [9] and this admixture results in the increase of intrinsic radioactive background. The purification of CsI from this admixture is especially difficult taking into account that ionic radii of Rb$^+$ and Cs$^+$ are close – 0.152 and 0.167 nm, respectively [10] and Rb is more isomorphic to Cs than K (0.138 nm) or Na (0.102 nm).

The experimental dependences of the concentrations and parameters describing the purification efficiency from the number of LTMC of CsI–H$_2$O system are presented in Fig. 3.

It should be noted that, although the dependence of Rb concentration in mother waters vs. N resembles the similar dependences for K and Na, the dependence of Rb concentration in the product is practically linear:

$$-\log c_{Rb} = 3.84(\pm 0.05) + \quad (8)$$
$$+ \ 0.148(\pm 0.01) \cdot N, \quad \beta = 0.71,$$

and authors of [11] estimated this parameter as ≈0.59.

So, the effective coefficient of purification of CsI from Rb is closer to 1 than in cases of K and Na that makes the purification by LTMC more difficult. As for α value it oscillates around of 0.1 (0.1÷0.15) that appreciably exceeds k_L parameter obtained

by Blank (0.06±0.02) [5]. After 6th LTMC the concentration of Rb becomes lower than the detection limit and this does not permit to perform correct estimations.

Distribution of Cu and Tl.

The behavior of these admixtures is considered together due to two reasons. The first one consists in the fact that both cations (Cu^+ and Tl^+) are precipitated by iodide ion as insoluble iodides, therefore, these admixtures should be accumulated in the solid phase during LTMC process. Other common feature is that the precipitated iodides can dissolve in solutions of alkali metal iodides forming iodide complexes: CuI_2^- and up to TlI_4^{3-}, respectively and the complexes of Cu are considerably stronger than Tl ones. The latter reason should lead to the accumulation of these admixtures in the mother waters.

Cu admixture is extremely harmful for the CsI-based scintillators since it affects the luminescent properties of the said materials. Authors of [12] showed that addition of $5\cdot10^{-6}$ wt. % of CuI into the growth melt led to the formation of complex centers which distribution in the crystals is non-uniform due to non-isomorphism of Cu^+ and Cs^+ (Cu^+ was considered as isomorphic to Na^+ [13]). The luminescence spectrum of CsI with $1\cdot10^{-6}$ wt. % of Cu contains an emission band with the maximum at 390 nm. The rise of Cu^+ concentration to $2\cdot10^{-4}$ wt. % results in the shift of the maximum position to 620 nm. Concentrations of Cu in CsI higher than $2\cdot10^{-5}$ wt. % cause the decrease of the light yield by 30 % [12].

As to the behavior of Cu^+ in the iodide solution, CuI is practically insoluble in water and the index of the solubility product ($pK_{s,CuI}$):

$$CuI \downarrow \rightleftarrows Cu^+ + I^- \qquad (9)$$
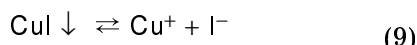
is equal to 11.96 [4]. CuI is dissolved in the excess of soluble iodides forming complexes:

$$Cu^+ + 2I^- \rightleftarrows [CuI_2]^-, \ \log b_2 = 8.85, \qquad (10)$$
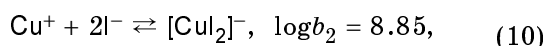
where b_i the instability constant of the complex with i ligands. Ditto, copper (I) can form dimers of Cu_2^{2+} composition even in the diluted solutions and this trend is also observed even in molten salts [14]. So, the efficiency of Cu admixture displacement from CsI at LTMC is dependent on the concurrence of the precipitation and complexing processes. The dependences of LTMC pa-
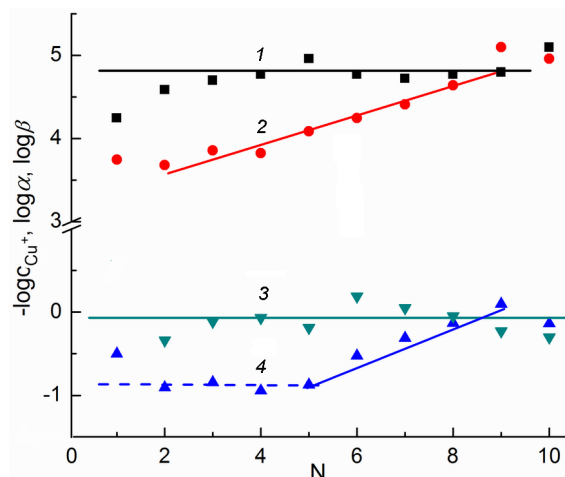

Fig. 4. The dependences of logarithm of Cu concentration ($-\log c_{Cu}$) in product (*1*), mother waters (*2*) and logarithms of thermodynamic (α) and effective (β) purification coefficients on numbers of LTMC cycles (*N*).

rameters vs. the number of cycles is presented in Fig. 4.

As is seen, there are two sections in the dependence of Cu concentration in the product. The first section is typical for an admixture displaced into the mother waters during the crystallization:

$$-\log c_{Cu} = 4.17(\pm0.08) + \qquad (11)$$
$$+ 0.162(\pm0.02) \cdot N, \ \beta = 0.69.$$

After the 5th crystallization a plateau corresponding to $5\cdot10^{-5}$ wt. % of Cu arises. It can be supposed that this is the limit of Cu removal from CsI at LTMC. As for the purification coefficient, β values in the inclined section are close to 1 and α ones oscillate near 0.1 that agrees with [5].

So, the behavior of Cu resembles that of Rb. It can be concluded that for Cu admixture complexing but not precipitation is the prevailing for LTMC process. A certain effect is caused by the non-isomorphism of Cu^+ and Cs^+ ions.

Although TlI is insoluble in water (pK_s,TlI = 7.24), thallium admixture passes into the iodide wastes because of complexing of $TlI_i^{(1-i)}$ composition. These complexes are not so strong as those in the case of Cu ($\log b_1 = 1.41$, $\log b_2 = 1.82$, $\log b_3 = 2.0$, $\log b_4 = 1.60$ [4]). This leads to the assuming that the distribution of Tl during LTMC can differ from that of Cu. Indeed, from Tables 1 and 2 it can be seen that Tl concentration in the mother waters during multiple LTMC remains practically constant whereas the
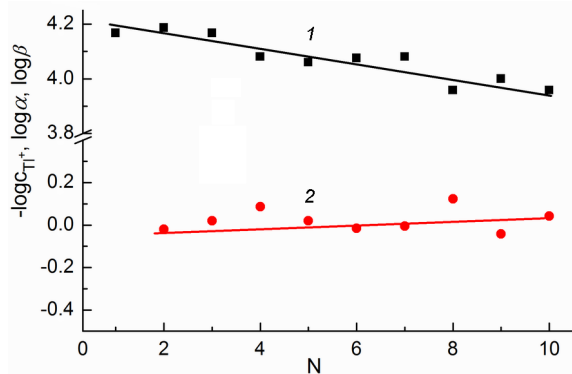
Fig. 5. The dependence of logarithm of TI concentration ($-\log c_{TI}$) in product (*1*) and effective purification coefficient (β) on numbers of LTMC cycles (*N*).
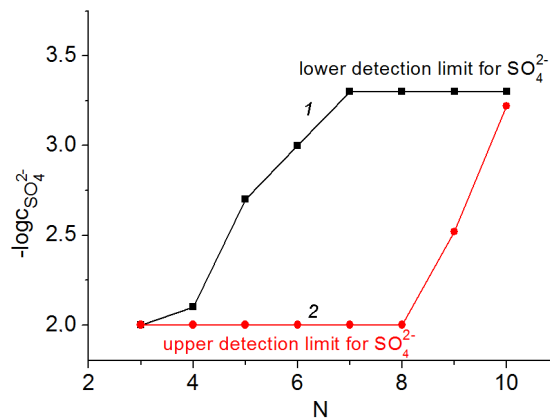

Fig. 6. The dependences of logarithm of SO_4^{2-} concentration ($-\log c_{SO4}{}^{2-}$) in product (*1*) and mother waters (*2*) on numbers of LTMC cycles.

amount of TI in the crystallized fraction somewhat increases as it is demonstrated by the dependence *1* in Fig. 5.

In contrast with the distribution of Na, K, Rb and Cu curve *1* for TI (see Fig. 5) possesses negative slope meaning that the multiple LTMC leads to the enrichment of the solid phase with thallium and the corresponding dependence can be approximated as

$$-\log c_{TI} = 4.21(\pm 0.02) - \qquad (12)$$
$$- 0.025(\pm 0.003) \cdot N, \quad \beta = 1.06.$$

So, the LTMC of the technogenic CsI solution did not lead to the displacement of TI from the crystallized fraction and TI is accumulated in the product. The low solubility of TII in water, weak stability of iodide complexes of TI and isomorphism of TI^+ and Cs^+ ions facilitate the accumulation of TI in the final product. It means that the crystallization methods do not permit to purify CsI solutions from TI up to the level necessary for the growth of pure CsI and the LTMC product could be used for the growth of CsI:TI single crystals.

To finish the consideration of the admixture distribution in CsI solutions during multiple LTMC let us stay on the distribution of sulfate ions. They are not referred to the isomorphic admixtures, therefore, their removal cannot be difficult. Ditto, the well-known technology of extra pure CsI production includes the chemical stage of sulfate separation using $Ba(OH)_2$, namely:

$$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4\downarrow. \qquad (13)$$

Further, the excess of $Ba(OH)_2$ is removed by Cs_2CO_3 excess and other alkaline

earth metal cations are also quantitatively removed.

The main source of sulfates in the liquid CsI wastes are the main water and products of commercial grease oil pyrolysis due to their possible entrance to the growth melt. The dependence of sulfate concentration in the product and mother waters are presented in Fig. 6. The data from the middle parts of the dependences can be approximated by the following equation:

$$-\log c_{SO_4^{2-}} = 0.62(\pm 0.3) + \qquad (14)$$
$$+ 0.39(\pm 0.05)\cdot N, \quad \beta = 0.41.$$

Since the deviation of the value of β from 1 is higher than for the other studied ions, sulfate ions can be removed from the technogenic CsI solution appreciably easier.

4. Conclusions

The very simple and suitable variation of the CsI wastes purification is proposed. It consists in the freezing of the wastes (38-40 wt. % solution of CsI) in 1.5 l PET bottles in the freezing chamber cooled to $-10°C$ with the following removal of 3–5 % of mother waters. The way permits to purify CsI to the extra pure quality by 10−11 LTMC cycles.

Due to the considerable contamination of the technogenic wastes with sodium the removal of all the studied admixtures during 3 initial cycles is essentially slower than during the following crystallizations. The threshold position corresponds to $5\cdot10^{-2}$ wt. % of Na in the CsI solution.

Analysis of α and β coefficient shows that $\alpha \neq \beta^2$ at multiple LTMC (the ideal cascade condition). Therefore, the product

from the n LTMC stage should be united with the mother waters from the $n+4$ stage of LTMC.

The purification coefficients for the main admixtures are estimated. For Na β value is 0.6–0.7 for the initial CsI solution and decreases to 0.35–0.5 for more pure solutions. The corresponding values for K are 0.75 and 0.5–0.55, for Rb β changes is 0.65–0.75 range. The value β for Cu is closer to 1 than corresponding parameters for alkali metal cations (excluding Rb) since CuI is insoluble in water and partially enters in the solid phase. Nevertheless, the strong complexing with iodide ions favors the displacement this admixture in the mother waters. For Tl β somewhat exceeds 1 that leads to the accumulation of this admixture in the product. This is caused by the isomorphism of Tl^+ to Cs^+ ions, the low solubility of TlI in water and relatively weak complexing of Tl^+ with iodide ions. The displacement of sulfate ions at LTMC is the simplest among the considered admixtures since SO_4^{2-} ions are non-isomorphic to the constituent ions of CsI.

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