ISSN 1066-3622, Radiochemistry, 2015, Vol. 57, No. 1, pp. 55–60. © Pleiades Publishing, Inc., 2015.
Original Russian Text © D.N. Shishkin, A.S. Il'in, S.A. Rodionov, A.N. Viznyi, 2015, published in Radiokhimiya, 2015, Vol. 57, No. 1, pp. 48–52.

Partitioning of REE(III) and TPE(III) with an Extractant Based on Chlorinated Cobalt Dicarbollide and Polyethylene Glycol

D. N. Shishkin*, A. S. Il'in, S. A. Rodionov, and A. N. Viznyi

Khlopin Radium Institute, 2-i Murinskii pr., St. Petersburg, 194021 Russia
** e-mail: dn.shishkin@mail.ru*

Received March 26, 2014

Abstract—Theoretical principles and practical characteristics are reported for an extraction process for REE and TPE partitioning using an extractant based on chlorinated cobalt dicarbollide (CCD) and polyethylene glycol (PEG). Joint extraction of REE and TPE is performed from a ≤1 M HNO_3 solution with a solution of CCD and PEG in a polar diluent. The TPE stripping is performed with an aqueous solution of a complexing agent (diethylenetriaminepentaacetic acid) and an organic base (urea or thiourea). Trials on an extraction rig in Gatchina showed that the process can be successfully used for exhaustive recovery of REE and TPE from real Purex process raffinates and for their subsequent partitioning, with reaching the required process parameters. The results of semicommercial trials of the REE/TPE partitioning process on the extraction installation of the Mayak Production Association are reported. The trials were performed on such scale for the first time in the world. In reprocessing of 40 m^3 of high-level raffinates, good results were obtained with respect to the process hydrodynamics, REE/TPE partitioning, and their separation from impurity elements. The process has high potential for use in HLW reprocessing technologies at new radiochemical plants.

Keywords: rare-earth elements, transplutonium elements, chlorinated cobalt dicarbollide, polyethylene glycol, extraction, partitioning

DOI: 10.1134/S1066362215010087

Russia follows the concept of the closed fuel cycle and partitioning of high-level waste (HLW) [1], in accordance with which HLW after the recovery of fissile materials from the spent nuclear fuel should be partitioned into fractions to ensure their subsequent safe and economic storage, disposal, or transmutation. In addition, an important problem is the recovery of valuable elements from HLW for their subsequent use for the production of sources of heat (^{90}Sr) or ionizing radiation (^{137}Cs), or for incorporation into NPP fuel (Am, Np). The waste should be partitioned into the TPE and REE fractions and the fraction containing long-lived Cs and Sr isotopes.

For this purpose, a process has been developed at the Radium Institute for extraction partitioning of wastes, with a solution of chlorinated cobalt dicarbollide (CCD) and polyethylene glycol (PEG) in a polar diluent used as solvent.

Cobalt dicarbollide, belonging to the class of metallocarboranes and having the formula $[(C_2B_9H_{11})_2Co]^-$ [2], was synthesized for the first time in the 1960s by M.F. Hawthorne et al. from the University of California and initially found no practical use. In the 1970s, Dr. M. Kyrš et al. from the Nuclear Research Institute (NRI, former Czechoslovakia) suggested using it for the extraction recovery of cesium (and later also of strontium) from acid solutions. The subsequent joint studies performed by researchers from NRI and Khlopin Radium Institute (RI) allowed the development of the technology and start (for the first time in the world) of the commercial recovery of Cs and Sr isotopes at the Mayak Production Association from acidic high-level wastes accumulated in the course of accomplishing defense programs and reprocessing irradiated fuel from WWER-440 (440-MW water-cooled water-moderated energy reactor) reactors. By 2007, when the technology was stopped after 10-year operation because of the lack of CCD stock and problems with financial support and production of new CCD

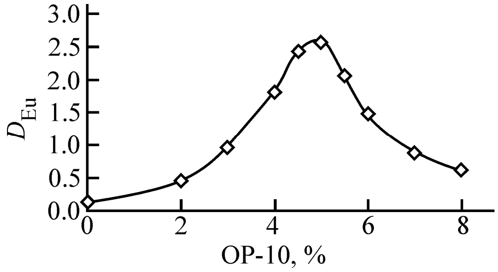

Fig. 1. Influence of the concentration of polyethylene glycol OP-10 in the solvent on the Eu distribution. Solvent: 0.25 M CCD in MNBTF. Aqueous phase: 1 M HNO_3.

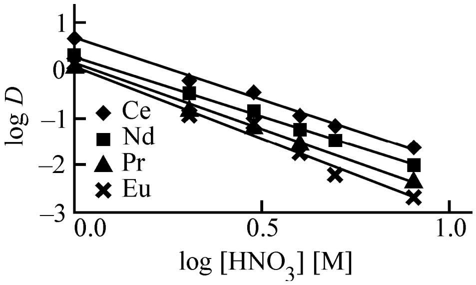

Fig. 2. Influence of the HNO_3 concentration on the REE distribution. Organic phase: 0.28 M CCD and 6% PEG in nitrobenzene.

batches, more than 1500 m^3 of such wastes with the β-activity exceeding 5×10^7 Ci had been reprocessed [3].

The process was performed with a chlorinated derivative of cobalt dicarbollide (CCD), containing 6–7 Cl atoms in the molecule and exhibiting extremely high radiation and chemical resistance.

Simultaneously with the development of a process for recovering Cs and Sr isotopes from HLW, studies were performed at RI and NRI with the aim of developing a process for the recovery of REE and TPE fractions from HLW and for the REE/TPE partitioning [4–9].

The studies have shown that joint recovery of REE and TPE from HLW is possible at the CCD concentration in the solvent close to 0.3 M and the HNO_3 concentration in the feed decreased to <1 M [10, 11].

The extraction of REE and TPE from nitric acid solutions occurs by the cation-exchange mechanism in accordance with Eqs. (1) and (2):

$$Me^{3+} + PEG(o) + 3HCCD(o) = MePEG(CCD)_3(o) + 3H^+(aq), \quad (1)$$

$$H^+(aq) + PEG(aq) = H^+PEG(o). \quad (2)$$

The metal cation or cationic complex of the metal with polyethylene glycol replaces the proton of the acid H^+CCD^- in the organic solution, displacing it into the aqueous phase. A specific feature of this system is strong dissociation of the acid and CCD salts in the organic phase.

With an increase in the polyethylene glycol concentration in the solvent, the REE distribution ratio passes through a maximum (Fig. 1), which is caused by competition of the metal complexes and protonated PEG complex in the organic phase [11].

REE and TPE can be readily stripped with 3–4 M HNO_3 solutions. REE and TPE are not noticeably separated in the extraction and acid stripping steps because of close distribution ratios of the elements of the REE and TPE series (Fig. 2).

With an increase in the REE(III) atomic number, the extractability slightly decreases, and the separation factors of the adjacent elements remain constant. The highest separation factor is observed for the Ce(III)/Eu(III) pair and does not exceed 3 [13].

The series of REE(III) extractability with CCD is opposite to the series of their extractability with organophosphorus acids, because here the degree of extraction recovery is primarily determined by the degree of hydration of the cation or its PEG complex, rather than by the strength of bonding of the REE cation with the acid anion.

In laboratory experiments, 2-mL portions of the organic and aqueous phases were contacted manually in test tubes for 5 min. The phases were analyzed for the REE and TPE content after centrifugation. ^{144}Ce, ^{154}Eu, and ^{241}Am were used as radioactive tracers. The aliquots of the organic and aqueous phases were analyzed on a γ-ray spectrometer or on an inductively coupled plasma mass spectrometer [11].

For REE/TPE partitioning, the use of the stripping solution of the TALSPEAK process [12], a solution of an aminopolycarboxylic acid (DTPA) and a hydroxy acid (lactic), was initially suggested, because organophosphorus acids for which the TALSPEAK process was developed extract REE(III) and TPE(III) by the cation-exchange mechanism, as CCD does.

An increase in the concentration of lactic acid (HLac) in the presence of DTPA only slightly decreases the Am(III) distribution ratio in the system (Fig. 3), in contrast to the TALSPEAK process. This result can be attributed to considerably larger amount

Table 1. Distribution ratios of REE(III) and Am(III) in relation to the initial aqueous phase composition

Initial aqueous phase composition, g L^{-1}					Equilibrium pH	Distribution ratio		
DTPA	methylamine	HLac	NaOH	NH_4OH		Ce(III)	Eu(III)	Am(III)
1	35				2.6	0.63		<0.045
3	35				2.6	0.21		<0.03
2		30	20			0.75		0.018
2		30	15		2.1	27		0.29
2				5	1.9	33	7.9	6.2
2				7	1.9	10.8	0.1	0.07

of free protons in the system with CCD because of significant dissociation of the acid H^+CCD^-, decreasing the complexing ability of DTPA in the organic phase.

To decrease the amount of free protons in the organic phase, addition of bases (both organic and inorganic) to the TPE stripping solution was suggested [11]. Introduction of a complexone in combination with an organic base into the extraction system allows REE/TPE partitioning (Table 1).

In some cases, high separation factors of Ce(III) and Am(III) were reached ($\beta_{Ce/Am} = 150$). However, the aqueous solution compositions given in the table appeared to be inconvenient from the viewpoint of hydrodynamics of the extraction process: They did not ensure sufficiently fast phase separation, and in some cases interfacial formations appeared.

Aqueous solutions containing DTPA and urea or thiourea appeared to be the best from the viewpoint of hydrodynamics and REE/TPE partitioning (Fig. 4).

In the system with the urea–DTPA stripping solution (Fig. 5), the REE distribution ratios monotonically decrease from La to Eu, then slightly decrease in going to Tb, and are approximately equal for heavy REE. The distribution of Am and Cm is similar to that of heavy REE. This fact indicates that efficient REE/TPE partitioning on a small number of extraction steps can be reached only for light REE. Heavy REE are not separated from TPE under these conditions. This system is convenient for HLW partitioning, because the content of light REE in HLW is considerably higher than the content of heavy REE [11].

A specific feature of this extraction system is high solubility of the complexone (DTPA) in the organic phase, which also favors the REE/TPE partitioning.

The separation factor of REE from Am(III) and Cm(III) decreases from ~1000 to 1.2 in the series La–Dy; therefore, Am(III) and Cm(III) can be readily

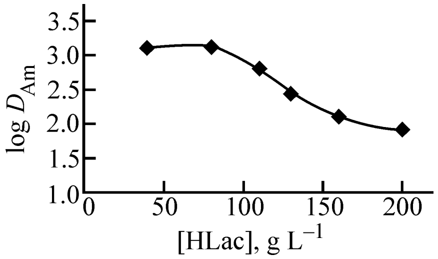

Fig. 3. Effect of lactic acid (HLac) on the Am distribution. Aqueous phase: 10 g L^{-1} DTPA, pH 2.2–2.4. Organic phase: 0.28 M CCD, 6% PEG in nitrobenzene.

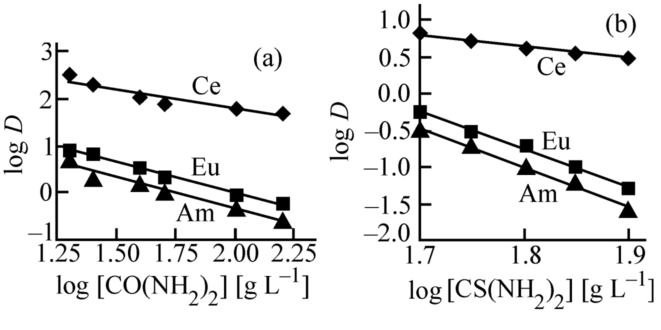

Fig. 4. Effect of (a) urea and (b) thiourea on the separation of REE(III) and Am(III). Aqueous phase: 2 g L^{-1} DTPA. Organic phase: 0.28 M CCD and 6% OP-10 in MNBTF.

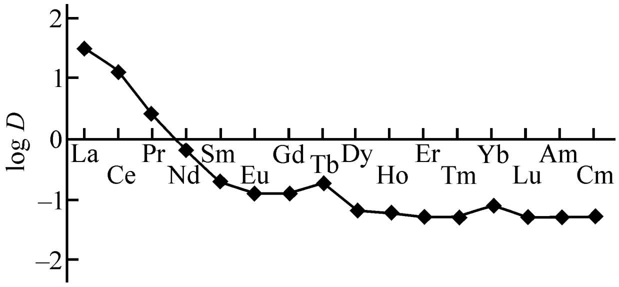

Fig. 5. Distribution ratios of REE(III), Am(III), and Cm(III). Aqueous phase: 10 g L^{-1} DTPA and 100 g L^{-1} urea. Organic phase: 0.3 M CCD and 6% OP-10 in MNBTF.

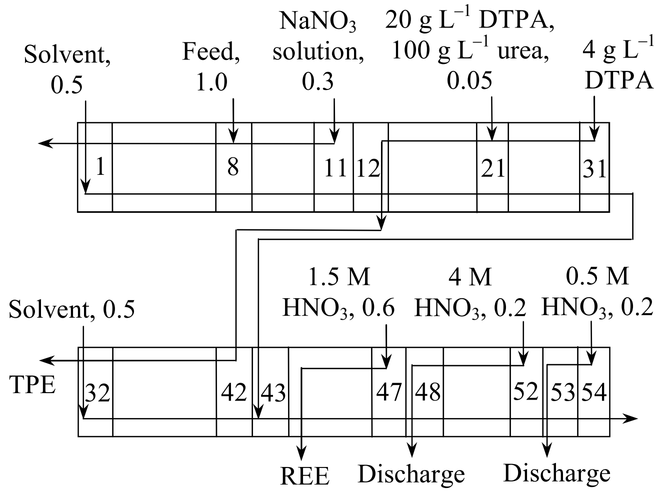

Fig. 6. Flowsheet of REE/TPE extraction partitioning on a rig in a hot cell of the radiochemical building of RI in Gatchina.

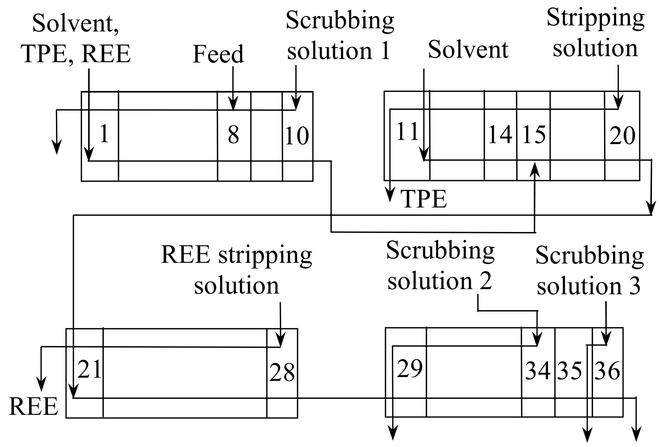

Fig. 7. Flowsheet of the REE/TPE extraction partitioning on installation 35-71.

separated from La, Ce, and Nd. The separation from Sm, Eu, Gd, and Tb is more difficult, and the separation from heavy REE is unfeasible.

The trials of the partitioning process were performed on the extraction rig assembled in hot cells of the radiochemical building of RI in Gatchina. Both simulated and real high-level Purex process raffinates were used as the feed [13].

One of the flowsheets used in laboratory trials of the extraction partitioning of REE and TPE is shown in Fig. 6.

Trials were performed in contactors of mixer–settler type with ejection mixing and transport of phases. The mixing chamber volume in one step of the contactor was 30 cm^3, and the settling chamber volume was 100 cm^3.

The raffinate from the first cycle of the Purex process after evaporation with acid distillation, dilution, and preliminary recovery of Cs and Sr radionuclides was used as the feed. The solution activity was 4 × 10^{10} Bq L^{-1}, and the HNO_3 concentration was 0.7 M.

The reprocessing of 35 L of the high-level solution resulted in more than 99.95% recovery of Am and Cm into the extract. More than 91% of stable REE isotopes and 0.0001% of α-emitters relative to their content in the feed passed to the REE strip. The separation factor of REE from α-emitters was 10^6. This value exceeds by a factor of 20 the value required for the arrangement of solidified REE in near-surface repositories (permissible content of TPE in the solidified REE strip 1 Ci t^{-1}). The total loss of TPE with the raffinate, REE strip, and scrubbing solutions did not exceed 0.006%. The separation factor of TPE from REE was 30 [13].

Laboratory studies and rig trials on REE/TPE partitioning were followed by the large-scale trials on commercial extraction installation 35-71 of the Mayak Production Association [14].

The extraction installation consisted of batteries of mixer–settler contactors with phase mixing by pulses of compressed air, of vessels, and of the dosing equipment. The maximum productive capacity of the installation with respect to the sum of the organic and aqueous phases was about 300 L h^{-1}. The scheme of the streams of the aqueous solutions and solvent in trials on the 35-71 installation is shown in Fig. 7.

Prior to the experiment, the feed was pretreated as follows. The raffinate after the recovery of U, Pu, and Np from the spent fuel of WWER-440 reactors by extraction with TBP was evaporated by a factor of several times to decrease the solution volume and then was diluted with water to an HNO_3 concentration of 3 M. The Cs and Sr radionuclides were preliminarily recovered from this solution on the same extraction installation with the extractant based on CCD and PEG. This was done for simplifying the flowsheet of the extraction partitioning of REE and TPE, because Cs and Sr in the step of REE and TPE extraction pass into the organic phase, and a special operation is required for their stripping.

The raffinate after the extraction of Cs and Sr was again diluted with water to an HNO_3 concentration of 0.5 M and was used as the feed in the REE/TPE partitioning technology. The feed composition is given in Table 2.

A solution of 0.28 M CCD and 6% OP-10 in *m*-nitrobenzotrifluoride (MNBTF) was used as solvent. The compositions and flow rates of solutions fed to the contactor are given in Table 3.

As a result of trials, 40 m^3 of the high-level solution was processed, and 10 m^3 of TPE concentrate and 9.7 m^3 of REE concentrate were obtained. The degree of recovery of TPE into the solvent exceeded 98%. The direct yield of TPE into the strip was 97%.

The second extraction cycle was performed on the same installation for still higher TPE preconcentration and for the removal of urea and DTPA from the solution. In this step, the TPE concentrate from the first extraction cycle was used as the feed. Nickel nitrate was added to this solution to a concentration of approximately 1 g L^{-1} for binding DTPA and displacing TPE from the DTPA complex. A 2 M HNO$_3$ solution was used in this cycle as the TPE stripping solution. As a result, 2.4 m^3 of TPE concentrate containing 230 g of Am isotopes and 21 g of Cm isotopes was obtained.

The composition of the TPE concentrate obtained and the separation factors of TPE from stable and radioactive impurities are given in Table 4.

During the 1-month trials, the solvent passed 24 cycles without deterioration of the parameters of the hydrodynamics, REE and TPE recovery, and their separation from the impurities. The productive capacity of the installation was close to the maximum designed level. The loss of Cm and Am with the outflowing aqueous solutions in two cycles did not exceed 4%.

The design of the RT-2 plant, developed in the 1990s, involved the technology of HLW partitioning using a CCD-based extractant. The recovery of the Cs + Sr and REE + TPE fractions was provided for. The technology involved 2–3-fold dilution of the feed prior to the extraction, which considerably increased the volume of the solution being processed.

The new technology developed at the Radium Institute for the extraction reprocessing of SNF, intended for trials at the Experimental and Demonstration Center (EDC) in Zheleznogorsk, involved obtaining the raffinate with an HNO$_3$ concentration of approximately 0.5 M. This acidity of the solution allows direct recovery of long-lived fission products and TPE from it by

Table 2. Feed composition

Radioactive isotopes		Other components	
isotope	content, GBq L^{-1}	component	concentration, mg L^{-1}
^{241}Am	1.1	Fe	220
^{243,244}Cm	2	Ni	40
^{125}Sb	6.4	Cr	30
^{144}Ce	19.4	Ca	600
^{106}Ru	17.8	Al	210
^{154}Eu	7.1	Y	30
$\sum\alpha$	4.4	∑REE	720
$\sum\beta$	48	HNO$_3$	0.5 M

Table 3. Compositions and flow rates of products

Product name	Solution composition	Flow rate, L h^{-1}
Feed	See Table 2	70
Solvent for REE and TPE recovery	0.28 M CCD and 6% OP-10 in MNBTF	70
Solvent for TPE strip scrubbing	0.28 M CCD and 6% OP-10 in MNBTF	8
Scrubbing solution 1	0.5 M HNO$_3$, 1 g L^{-1} H$_2$C$_2$O$_4$	10
TPE stripping solution	15 g L^{-1} DTPA, 150 g L^{-1} urea	20
REE stripping solution	1.5 M HNO$_3$	15
Scrubbing solution 2	0.5 M HNO$_3$	30
Scrubbing solution 3	0.05 M HNO$_3$.	15

Table 4. Composition of TPE concentrate

Component	Content	Separation factor from TPE
^{241}Am	12 GBq L^{-1}	
^{243,244}Cm	2.7 GBq L^{-1}	
^{125}Sb	0.23 GBq L^{-1}	1200
^{106}Ru	1.4 GBq L^{-1}	300
HNO$_3$	1.8 M	
Ca	50 mg L^{-1}	60
Fe	30 mg L^{-1}	60
Ni	160 mg L^{-1}	30
Cr	10 mg L^{-1}	60
Al	30 mg L^{-1}	30
La	100 mg L^{-1}	100
Ce	10 mg L^{-1}	120
Pr	30 mg L^{-1}	80
Nd	50 mg L^{-1}	100
Sm	30 mg L^{-1}	180
Eu	20 mg L^{-1}	12
Y	20 mg L^{-1}	25
∑REE	150 mg L^{-1}	90

extraction with CCD without preliminary complex pretreatment (denitration, evaporations with acid distillation) or dilution, and also complete HLW partitioning with the separation of the REE and TPE fractions.

There are still no processes in the world for HLW partitioning with separation of the REE and TPE fractions, tested on such a large scale and ready for commercial use with real high-level solutions. We believe that the potential of technologies with CCD is far from being exhausted, and such technologies can find use in the development and designing of new radiochemical processes.

REFERENCES

1. *Strategiya razvitiya atomnoi energetiki Rossii v pervoi polovine XXI veka* (Strategy of the Development of Atomic Power Engineering in Russia in the First Half of the XXI Century), Moscow: TsNIIatominform, 2001.
2. Grimes, R.N., *Carboranes*, New York: Academic, 1970.
3. Gromov, G.V., Dzekun, E.G., Domnin, V.V., et al., Abstracts of Papers, *Chetvertaya Rossiiskaya konferentsiya po radiokhimii "Radiokhimiya-2003"* (Fourth Russian Conf. on Radiochemistry "Radiochemistry-2003"), Ozersk, 2003, pp. 182–183.
4. Rais, J. and Gruner, B., *Ion Exch. Solvent Extr. Ser. Adv.*, 2004, vol. 17, pp. 243–387.
5. Vanura, P., Jedinakova, V., and Juklikova, I., *Solvent Extr. Ion Exch.*, 1994, vol. 2, no. 2, pp. 439–458.
6. Rais, J. and Tachimori, S., *Sep. Sci. Technol.*, 1994, vol. 29, no. 10, pp. 1347–1365.
7. Shishkin, D.N., Lazarev, L.N., Dzekun, E.G., and Prokopchuk, Yu.Z., USSR Inventor's Certificate no. 305 289, December 1, 1989.
8. Shishkin, D.N., Lazarev, L.N., and Dzekun, E.G., RF Patent 2 026 819, January 11, 1991.
9. Shishkin, D.N., Kocharina, E.V., Galkin, B.Ya., et al., RF Patent 2 291 112, February 24, 2005.
10. Benesova, M., Kuca, L., Kyrs, M., et al., in *Management of Alpha Contaminated Wastes: Symp.*, June 2–6, 1980, Vienna, 1981, pp. 563–571.
11. Shishkin, D.N., *Cand. Sci. (Chem.) Dissertation*, Leningrad: Khlopin Radium Inst., 1989.
12. Weaver, B. and Kappelman, F.A., *J. Inorg. Nucl. Chem.*, 1968, vol. 30, pp. 263–272.
13. Shishkin, D.N., Viznyi, A.N., Galkin, B.Ya., et al., in *Khimiya i tekhnologiya ekstraktsii: Sbornik nauchnykh trudov RKhTU im. D.I. Mendeleeva. Materialy XII Rossiiskoi konferentsii po ekstraktsii* (Extraction Chemistry and Technology: Coll. of Scientific Works of the Mendeleev Russian Univ. of Chemical Technology. Proc. XII Russian Conf. on Extraction), Moscow, October 7–13, 2001, vol. 2, pp. 116–125.
14. Esimantovskiy, V.M., Galkin, B.Ya., Dzekun, E.G., et al., in *Int. Symp. "Waste Management-92,"* Tucson (USA), March 1–5, 1992, pp. 801–804.

Translated by G. Sidorenko