

Introduction

^{99m}Tc is extremely important for medical practice, and efforts to develop the best procedure for the production of its parent radionuclide, ⁹⁹Mo, for its subsequent use in technetium generators are being made for more than four decades. For this purpose, a composite ceramic target containing HEU dioxide and a filler metallic powder (Al, Mg, etc.) is irradiated in a high-flux reactor to obtain concentrate solution for fission Mo recovery by sorption, extraction or precipitation. However, this way has been restricted by IAEA because of nuclear nonproliferation and one of the options is to use irradiation of LEU dioxide without filler in commercial-level fluxes and to rise the concentration capability.

In this way extraction of Mo, U and certain FP from HNO₃ solutions with 0.2% solutions of higher hydroxamic acids (HA) in alcohols poorly soluble in water has been studied for ⁹⁹Mo concentrate production from solutions of different enriched U targets, including those of very low enrichment (3% ²³⁵U dioxide).

Experimental

Nitric acid solutions of molybdenum were prepared by dissolution of metallic Mo powder, and/or an acidified ⁹⁹Mo stock solution was used (specific activity 20 GBq·g⁻¹ Mo). The activity concentration of ¹²⁵I stock solution was 4.5 GBq·L⁻¹. Experiments on the extraction of Mo with HAs were performed in the following concentration ranges, M: Mo, from 1.25 to 5.7; HAs, from 9.4 to 27. These concentration ranges were varied depending on the experimental conditions.

Extraction experiments were performed in 15- and 50-mL test tubes. The phases were agitated for 1 min. with a Vortex laboratory vibration stirrer at a rotation rate of 3000 rpm, which was sufficient to attain the equilibrium.

The content of water-soluble hydroxamic acid in solutions was determined by spectrophotometry with Fe³⁺ in sulfuric acid. The content of metals in solutions was determined by ICP AES. The Mo concentration was determined by the standard colorimetric method with thiocyanate or by isotope dilution of ⁹⁹Mo with the measurement performed after the attainment of the radioactive equilibrium with ^{99m}Tc.

Results and discussion

Mo extraction

The extraction preconcentration of ⁹⁹Mo can be performed using solutions of poorly water-soluble HAs, namely benzo-, caprino- and laurylohydroxamic acids (BHA, CHA and LHA, respectively) in normal or branched alcohols C₅-C₁₀. The optimum solvent consists of CHA in *n*-decanol (see Table 1), because it ensures the highest distribution ratio of Mo among the alcohols tested and is characterized by the highest flash point and by low solubility in water. At the same time, the extraction of U is insignificant.

Dynamics of the Mo mass transfer shows (Fig. 1) that, in the case of LHA and CHA, which are poorly soluble in water, the equilibrium is reached later (in 60 s) than in the case of water-soluble BHA (~30 s). Presumably, BHA forms in the aqueous phase a complex with Mo which then passes into the organic phase. In the case of LHA and CHA, the formation of a complex occurs only at the interface by the first order reaction.

References

Table 1. Extraction of Mo and HNO₃ from 2 M HNO₃ with 9.4 mM solutions of HA in various alcohols at 20 °C and reference data for separate alcohols. Initial concentration in the aqueous phase: 1.25 mM Mo or 380 mM U.

Alcohols	M	r	C	T, °C		Sol. (20), mmol/L		Distribution coefficient												
				Boil.	Insin.	Alkanol. H ₂ O	H ₂ O Alkanol	HNO ₃	HA		HA (+Mo)		Mo into HA				U			
		kg m ⁻³	mol L ⁻¹								BHA	KHA LHA	BHA	KHA LHA	no HA	BHA	KHA	LHA	LHA	
3-methyl-1-butanol	88	813	9.2	132	43	267	250	~8500	0.38	1.2			5.0		0.60	100	80	90	0.18	
Cyclohexanol	100	962	9.6	161	61	39	-	~1200	0.52	1.3			1.8		0.52	160	90	130	0.23	
4-methyl-2-pentanol	102	808	7.9	133	46	78	-	~2500	0.33	1.7			5.5		0.15	120	140	120	0.09	
Pentanol-1	88	811	9.2	138	48	245	200	~8350	0.40	0.9			1.5		0.55	110	50	70	0.14	
Hexanol-1	102	820	8.0	156	60	59	50	~3200	0.28	1.4	>100		6.0	>100	0.47	120	60	80	0.09	
Heptanol-1	116	822	7.1	176	74	15	10	~2600	0.22	1.9			4.1		0.32	130	70	100	0.06	
Octanol-1	130	824	6.3	195	86	3.5	2.8	~2100	0.16	1.7			3.4		0.29	140	80	110	0.05	
Nonanol-1	144	827	5.9	212	96	0.95	0.62	~1800	0.13	1.2			3.2		0.25	150	90	120	0.05	
Decanol-1	158	830	5.2	232	130	0.32	0.20	~1570	0.07	1.1			2.1		0.22	160	100	130	0.04	

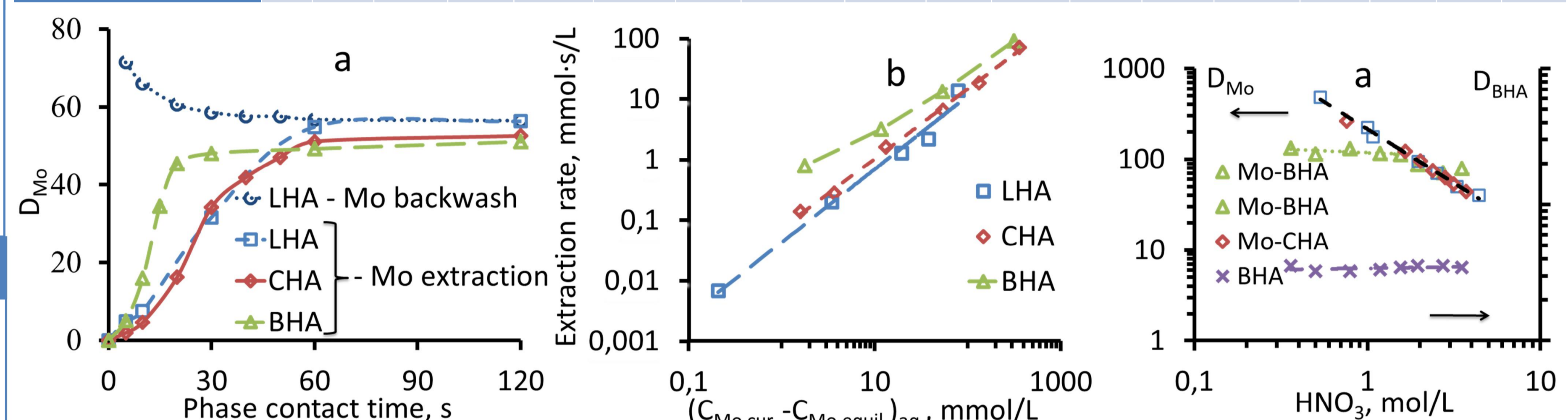


Fig. 1. Influence of the phase contact time on the stripping and extraction of Mo (a) and on the extraction rate (b). Solvent phase: 14 mM HA in decanol-1; equilibrium aqueous phase: 2 M HNO₃. Initial Mo solvent or aqueous concentration: 5.7 mM

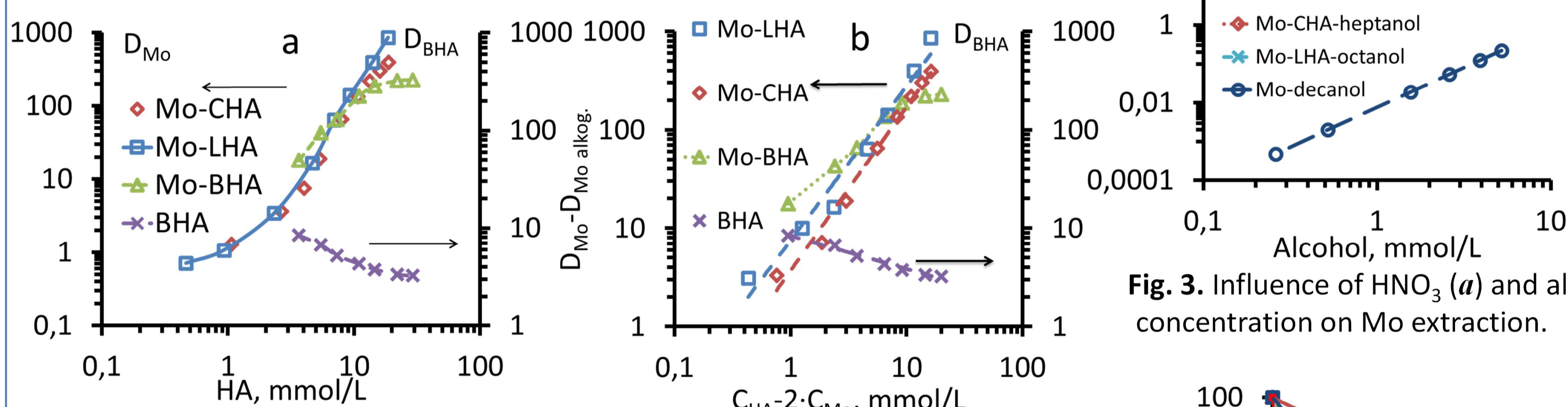


Fig. 2. Influence of the total (a) and free (b) HA concentration on Mo and BHA extraction. Solvent phase: HA in decanol-1; equilibrium aqueous phase: 2 M HNO₃; initial Mo concentration: 1.25 mM

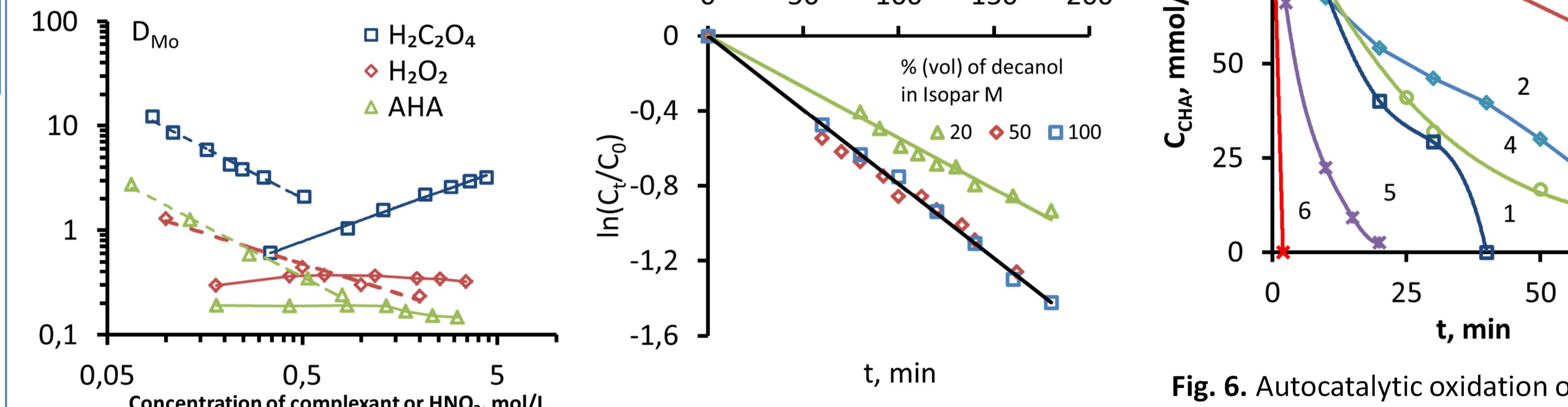


Fig. 4. Mo backwashing by solution of HNO₃ with complexant. Initial Mo solvent conc. 1.25 mmol/L. — 1 mol/L of complexant; - - - 2 mol/L HNO₃. Fig. 5. Hydrolysis of 0.1 mol/L CHA in the solvent containing decanol with Isopar M + 0.3 mol/L HNO₃

The Mo distribution ratio decreases as the HNO₃ concentration is increased (Fig. 2), which is typical of cation-exchange (salt-forming) processes. The log-log plot of D_{Mo} vs. total CHA or LHA concentration is slightly S-shaped, but it is linear with the slope of 2.0 for D_{Mo} without Mo extraction by alcohol vs. free HA concentration. D_{Mo} in the case of CHA (Fig. 3) is near indifferent for alcohol content, but has the slope of 1.0 for LHA.

Mo backwashing

As seen from Fig. 4, D_{Mo} distribution ratios decrease in inverse proportion to the square root of the ligand concentration in the case of using H₂O₂ and to the ligand concentration in the case of AHA and H₂C₂O₄. At the HNO₃ concentration increased over 1 mol/L the Mo distribution ratios in backwashing with AHA decrease in inverse proportion to the square root of the HNO₃ concentration, while the influence of the HNO₃ concentration on the Mo backwashing with the H₂O₂ solution is weak, and the total result is insufficient. That is why HA decomposition has been tested as well. The main way of HA decomposition in HNO₃ solutions, as well as in equilibrium alcohol phase, is hydrolysis (Fig. 5). At the temperature above 50 °C autocatalytic HA decomposition takes place in the case of BHA in both phases, as well as at their mixing. In the case of low water-soluble CHA the autocatalysis is realized at 70-80 °C only (Fig. 6) during the phase mixing at the tendency to attenuation with n=S/A phase ratio from 1 to 10. It is practically useful to combine both methods.

Rig trials

The flowsheet testing included dissolution of U-Al model or real targets in 8 mol/L HNO₃ containing 0.2 g/L Hg and 0.2 g/L HF at 95 °C, allowing further I₂ and Ru compounds air stripping in the special tests. The further concentrating process was tested in counter-current and batch variants and the latter (Fig. 7) was found to be rather effective.

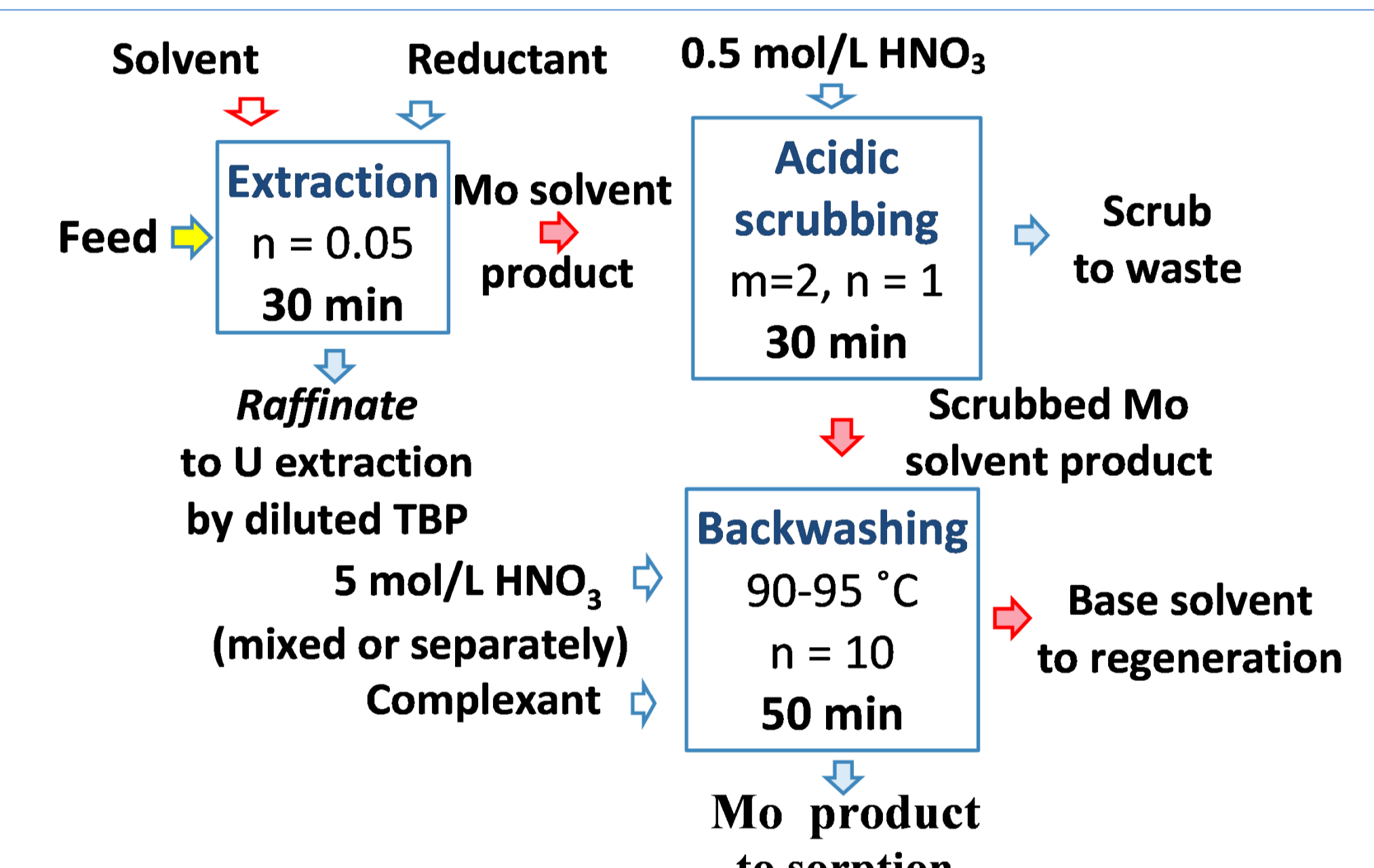


Fig. 7. Flowsheet for ⁹⁹Mo separation from dissolved LEU target using caprinohydroxamic acid dissolved in 20% n-decanol + Isopar-M. (n = Solv/Aq by volumes, m = number of contacts).

Mo extraction recovery was performed using 27 mmol/L CHA in 20% n-decanol with Isopar-M in 3 steps: extraction, scrubbing and backwashing - in the vessels of decreasing volume according to the concentrating factor. The simulate feed contained, mol/L: HNO₃ - 1,2; Al - 1,2; Fe - 5·10⁻³; U - 0,11; Hg - 1·10⁻³; ²³⁹Pu - 1,4·10⁻⁴; Mo - 3,2·10⁻⁵, as well as 15 MBq/L ⁹⁹Mo, 5,2 MBq/L ¹²⁵I and 4,1 MBq/L ²³⁹Np.

The achieved total concentrating factor was 180 at process duration 2 h. Decontamination factors were ~1.5·10⁶ from U, ~850 from ¹²⁵I, > 10⁵ from ²³⁹Pu, > 10⁶ from ²³⁹Np, > 10⁶ from Al, 4.6·10⁴ from Fe, ~2·10⁴ from Hg.

The feasibility study has indicated that the compact extraction flowsheet and simple batch equipment are suitable for profitable ⁹⁹Mo recovery from LEU (standart 3-5% ²³⁵UO₂) targets. Final Mo decontamination for Tc generator production can be performed by sorption and/or by sublimation.

We assume the method to be an interlocutory decision between HEU irradiation and that of Mo isotopes ⁹⁸Mo or ¹⁰⁰Mo.

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