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THE DISTRIBUTION OF SOME RARE METALS IN THE PROCESS OF SEPARATION OF ORGANIC MATTER FROM ESTONIAN DICTYONEMA ARGILLITE

In our previous works [1, 2] flow-sheets for beneficiation of argillites from Maardu and Toolse phosphorite deposits with the aim to obtain organic matter (OM) and pyrite concentrates have been presented. As is known [3, 4], these argillites contain several rare metals, of them uranium, molybdenum and vanadium being the most important due to their relatively high concentration in argillite, as well as to their potential commercial value and impact on the environment.

There exists a good relationship between U and OM, as well as Mo and OM [5]. Both the metals have a high negative correlation with quartz and pyrite. Vanadium has no such a strong affinity to OM as compared with Mo and U, while it has a positive correlation with clay minerals.

In this paper, the distribution of the above rare metals in the process of separation of OM from Maardu and Toolse argillites is discussed. The beneficiation process of argillite consists of the hydrocycling treatment, in the course of which OM is separated as a light fraction, followed by direct flotation of OM and pyrite concentrates. Determinations of Mo and U were made by X-ray fluorescence, V by titration and pyrite by titration of iron. OM was measured by loss by roasting, at that the forming of sulfate and iron oxide was taken into account.

Figs. 1 and 2 present flow-sheets for benefication of Maardu and Toolse argillites in which the distribution of Mo is demonstrated. Similar data on U and V are listed in Tables 1 and 2.

In the hydrocycling process of Maardu as well as Toolse argillite, the separation of Mo, U and V into the light fraction was considerable, the recovery being 70—75 %. In the following flotation of Maardu argillite (Fig. 1), the OM concentrate yield was 26.3 %. The recovery of Mo, U and V in this concentrate was 46.4, 46.4 and 28.5 % respectively. The residue from OM flotation underwent hydrocycling, the light fraction was redirected into the flotation process, while the heavy one was hauled to wastes. The recovery of Mo, U and V into waste was 9.9, 19.7 and 35.1 % respectively.

In the rougher flotation of Toolse argillite (Fig. 2), affording the OM concentrate in 43.6 % yield, the recovery of rare metals was 60 %. In each stage of the cleaner flotation, the OM concentrate was enriched in OM and rare metals. In the third stage of the cleaner flotation the yield of material was 34.3 % and the recovery of rare metals in the froth product 49—54 %. In the last stage of the cleaner flotation the OM concentrate, whose organic content was 61.5 %, in 12.9 % yield was separated. The content of rare metals in this concentrate was high, viz. 1008, 325 and 1790 g/t for Mo, U and V respectively, being augmented in comparison with feed material by a factor of 2.2, 2.0 and 1.6. Their recovery in this final concentrate was low, 21—29 %, because the underflow products in the cleaner flotation were not

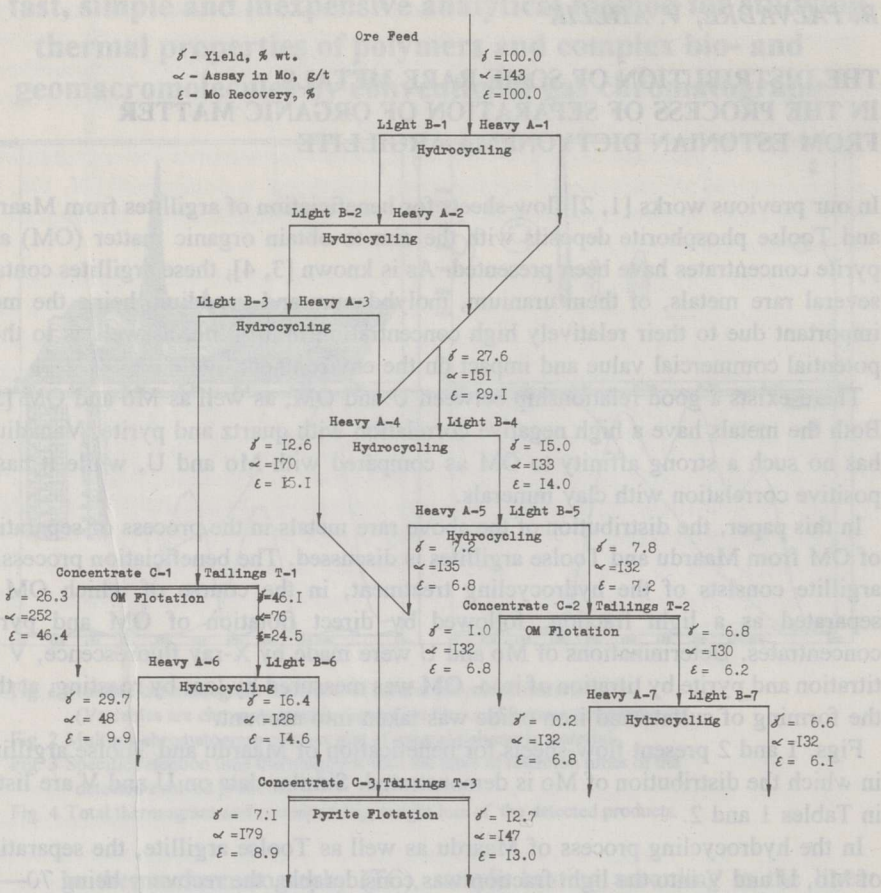

Fig. 1. Distribution of molybdenum on processing Maardu argillite

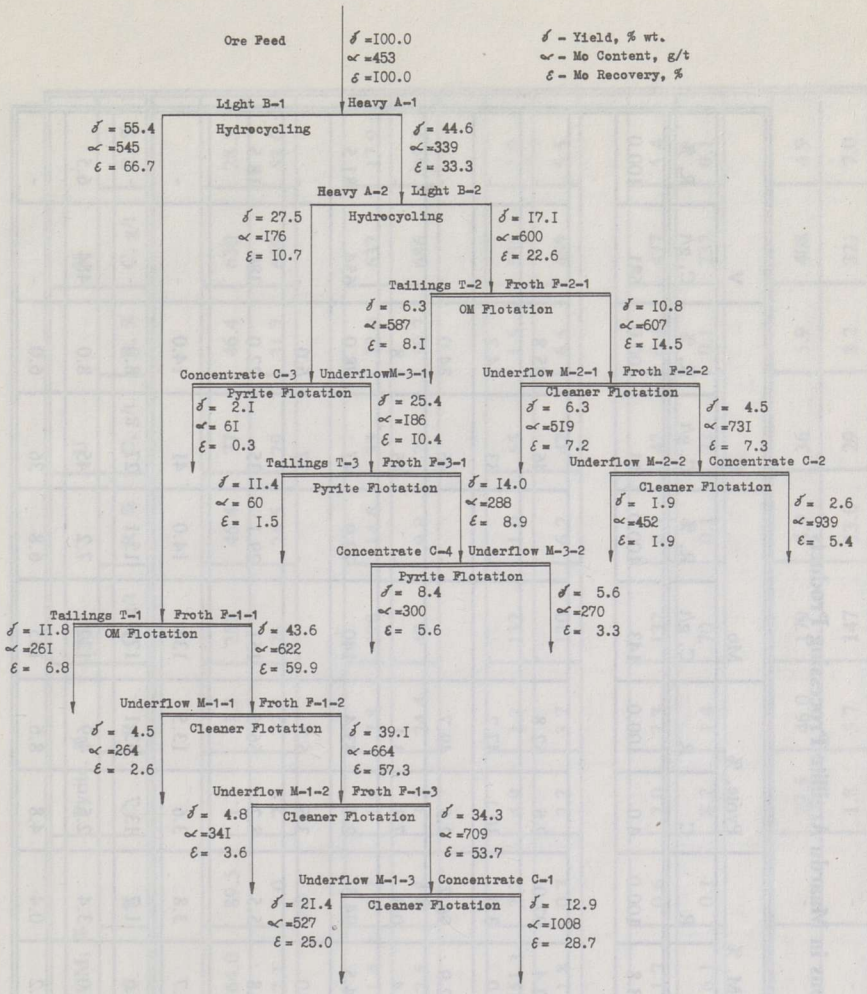

Fig. 2. Distribution of molybdenum on processing Toolse argillite

Table 1. **Rare Metals Concentrations in Maardu Argillite Processing Products**

Product	Yield, %	OM, %		Pyrite, %		Mo		U		V	
		C	R	C	R	C, g/t	R, %	C, g/t	R, %	C, g/t	R, %
Feed	100.0	18.8	100.0	4.0	100.0	143	100.0	44	100.0	681	100.0
Hydrocycling											
Light fraction B-1	81.3	22.4	97.0	2.6	52.8	-	-	46	85.8	-	-
Heavy fraction A-1	18.7	3.0	3.0	10.1	47.2	-	-	33	14.2	-	-
Light fraction B-2	79.6	22.9	96.7	2.5	49.7	-	-	46	84.0	-	-
Heavy fraction A-2	1.7	3.4	0.3	7.3	3.1	-	-	45	1.8	-	-
Light fraction B-3	72.4	24.5	94.5	2.4	43.4	140	70.9	47	78.0	654	81.5
Heavy fraction A-3	77.2	6.0	2.2	3.5	6.3	-	-	37	6.0	-	-
Total heavy fraction (A-1) - (A-3)	27.6	3.8	5.5	8.2	56.6	151	29.1	35	22.0	389	18.5
Light fraction B-4	15.0	4.7	3.8	3.6	13.5	133	14.0	41	14.0	-	-
Heavy fraction A-4	12.6	2.6	1.7	13.7	43.1	171	15.1	27	8.0	-	-
Light fraction B-5	7.8	8.0	3.4	2.5	4.9	132	7.2	45	8.0	484	6.5
Heavy fraction A-5	7.2	1.2	0.4	4.8	8.6	135	6.8	36	6.0	-	-

Table 1 (continued)

Product	Yield, %	OM, %		Pyrite, %		Mo		U		V	
		C	R	C	R	C, g/t	R, %	C, g/t	R, %	C, g/t	R, %
OM flotation I											
Concentrate C-1	26.3	64.0	89.5	1.7	11,2	252	46.4	77	46.4	630	28.5
Tailings T-1	46.1	2.1	5.0	2.8	32.2	76	24.5	29	31.7	669	53.0
Hydrocycling											
Light fraction B-6	16.4	1.4	1.2	1.9	7.8	128	14.6	33	12.0	637	17.9
Heavy fraction A-6	29.7	2.5	3.8	3.3	24.4	48	9.9	29	19.7	686	35.1
OM flotation II											
Concentrate C-2	1.0	51.1	2.7	4.9	1.2	132	1.0	65	1.5	585	1.0
Tailings T-2	6.8	1.8	0.7	2.2	3.7	130	6.2	42	6.5	469	5.5
Hydrocycling											
Light fraction B-7	6.6	1.7	0.6	2.0	2.3	132	6.1	42	6.4	477	5.4
Heavy fraction A-7	0.2	6.1	0.1	8.2	1.4	70	0.1	23	0.1	232	0.1
Pyrite flotation											
Concentrate C-3	7.1	-	-	29.5	46.0	179	8.9	36	5.9	408	4.9
Tailings T-3	12.7	-	-	1.8	5.7	147	13.0	29	8.2	321	7.0

C - content, R - recovery, "-" - not analysed, here and in Table 2.

Table 2. **Rare Metals Concentrations in Toolse Argillite Processing Products**

Product	Yield, %	OM, %		Pyrite, %		Mo		U		V	
		C	R	C	R	C, g/t	R, %	C, g/t	R, %	C, g/t	R, %
Feed	100.0	17.3	100.0	6.2	100.0	453	100.0	162	100.0	1105	100.0
Hydrocycling											
Light fraction B-1	55.4	24.1	76.9	1.0	13.0	545	66.7	212	72.5	1436	72.0
Heavy fraction A-1	44.6	9.0	23.1	12.5	87.0	339	33.3	100	27.5	693	28.0
Light fraction B-2	17.1	16.4	16.2	1.4	3.7	600	22.6	179	18.9	1253	19.4
Heavy fraction A-2	27.5	4.4	6.9	18.9	83.3	176	10.7	51	8.6	345	8.6
OM flotation I											
Froth F-1-1	43.6	29.5	74.1	1.7	12.0	622	59.9	232	62.4	1510	59.6
Tailings T-1	11.8	4.2	2.8	0.5	1.0	261	6.8	193	10.1	1162	12.4
Cleaner flotation											
Froth F-1-2	39.1	32.2	72.6	1.8	11.3	664	57.3	240	58.0	1540	54.5
Underflow M-1-1	4.5	5.9	1.5	1.0	0.7	264	2.6	166	4.4	1246	5.1
Froth F-1-3	34.3	36.0	71.2	1.9	10.6	709	53.7	253	53.5	1561	48.5
Underflow M-1-2	4.8	5.2	1.4	0.9	0.7	341	3.6	153	4.5	1381	6.0

Table 2 (continued)

Product	Yield, %	OM, %		Pyrite, %		Mo		U		V	
		C	R	C	R	C, g/t	R, %	C, g/t	R, %	C, g/t	R, %
Concentrate C-1	12.9	61.5	45.7	1.6	3.3	1008	28.7	325	25.8	1790	20.9
Underflow M-1-3	21.4	20.7	25.5	2.1	7.3	527	25.0	210	27.7	1423	27.6
OM flotation II											
Froth F-2-1	10.8	22.1	13.8	1.6	2.8	607	14.5	200	13.3	1289	12.6
Tailings T-2	6.3	6.6	2.4	0.9	0.9	587	8.1	145	5.6	1192	6.8
Froth F-2-2	4.5	36.6	9.5	1.9	1.4	731	7.3	229	6.3	1342	5.5
Underflow M-2-1	6.3	11.8	4.3	1.4	1.4	519	7.2	180	7.0	1251	7.1
Concentrate C-2	2.6	49.2	7.4	2.0	0.8	939	5.4	245	3.9	1260	3.0
Underflow M-2-2	1.9	19.6	2.1	1.8	0.6	452	1.9	209	2.4	1456	2.5
Pyrite flotation											
Concentrate C-3	2.1	-	-	97.8	33.3	61	0.3	9	0.1	128	0.2
Underflow M-3-1	25.4	-	-	12.4	50.0	186	10.4	54	3.5	365	8.4
Tailings T-3	11.4	-	-	0.6	1.1	60	1.5	40	2.8	100	1.0
Froth F-3-1	14.0	-	-	21.9	48.9	285	8.9	67	5.7	584	7.4
Concentrate C-4	8.4	-	-	34.5	47.2	300	5.6	84	4.3	587	4.5
Underflow M-3-2	5.6	-	-	1.9	1.7	270	3.3	45	1.4	563	2.9

See footnotes to Table 1.

redirected into the flotation process, they were subjected to analysis. As can be seen, the OM content of the mineral phase in the final flotation stage was high, 20.7 %, as was that of rare metals. The V content of the mineral phase increased especially regularly in the cleaner flotation process. At the same time, the recovery of Mo, U and V in the mineral waste was 7—12 %, being the highest for V.

In the hydrocycling process of Maardu as well as of Toolse argillite, 25—30 % of rare metals were separated into the heavy fraction. After its additional hydrocycling the light fraction obtained was involved in the flotation of OM. In this process the OM concentrate was separated with the recovery of 1.0 and 6.3 % for Maardu and Toolse argillite respectively. The recovery of rare metals in this concentrate was 1—1.5 and 3—5 % for Maardu and Toolse argillite respectively.

Table 3. **Recovery of Rare Metals in the Waste Removed**

Material	Yield, %	Recovery, %		
		Mo	U	V
Maardu				
Mineral tails of OM flotation I	29.7	9.9	19.7	35.1
Mineral tails of OM flotation II	0.2	0.1	0.1	0.1
Pyrite concentrate	7.1	8.9	5.8	4.9
Pyrite flotation tails	12.7	13.0	8.2	7.0
Total	49.7	32.9	33.8	47.1
Toolse				
Mineral tails of OM flotation I	11.8	6.8	10.1	12.4
Mineral tails of OM flotation II	6.3	8.1	5.6	6.8
Pyrite concentrate	2.1	0.3	0.1	1.0
Fine pyrite concentrate	8.4	5.6	4.3	4.5
Pyrite flotation tails	11.4	1.5	2.8	0.2
Total	40.0	22.3	22.3	24.9

In Maardu argillite fine-grained pyrite is associated with quartz and clay minerals [6] and the recovery of pyrite in the flotation concentrate was only 29.5 %. The recovery of Mo, U and V in this pyrite fraction was 5—9 % and in the mineral tails 7—13 %.

Unlike Maardu argillite, the pyrite of Toolse argillite is represented mainly by macrocrystals and concretions. So, in the first stage of flotation pure pyrite was obtained (assay in pyrite 97.8 %). By further flotation fine-dispersed pyrite was separated (assay in pyrite 34.5 %). The tails from the flotation were mostly pure quartz. The concentrations of Mo, U and V in pure pyrite and quartz were low and their recoveries in these fractions negligible, 0.1—2.8 %. In the fine-dispersed pyrite concentrate the recovery of rare metals was 4.5—5.6 %.

In argillite processing the mineral tails from both the flotation processes of OM (in case of Maardu argillite after additional hydrocycling), the pyrite concentrate and the tails from pyrite flotation (in case of Toolse argillite quartz) were removed to wastes. Upon Maardu argillite processing the recovery of rare metals in these removed tails was high (33—48 %, see Table 3) due to their augmented recovery in the pyrite fraction impregnated with clay minerals (12—22 %) and their increased recovery in the mineral phase.

On processing Toolse argillite, the separation of pyrite was more exhaustive than on processing Maardu argillite, the total recovery of rare metals in waste was 22—25 %. The total yield of the latter, consisting of the flotation tails and pyrite concentrates, was 40.0 %. 20—26 % of rare metals was distributed in intermediate flotation products and their recovery in further processing will be possible.

Table 4. **Enrichment Factor *Ü* of Rare Metals in the Beneficiation of Toolse Argillite**

Material	Mo	U	V
Light hydrocycling fraction B-1	1.20	1.31	1.30
Heavy hydrocycling fraction A-2	0.39	0.31	0.31
OM flotation concentrate C 1—4	2.23	2.01	1.62
OM flotation tailings T-1	0.58	1.19	1.05
Pyrite flotation concentrate C 3—1	0.13	0 06	0.12
Pyrite flotation tailings T-3	0.13	0.25	0.09
Pyrite flotation concentrate C 3—2	0.66	0.21	0.53

To evaluate the distribution of rare metals in different products of argillite beneficiation process, the enrichment factor of rare metals in the fractions, I, can be calculated:

$$I = C_i/C_f$$

where C_i and C_f are metal concentration in the fractions separated and the feed material respectively.

The data presented in Table 4 show that rare metals were upgraded in the OM concentrate and the light hydrocycling fraction, while their concentrations in the heavy hydrocycling fraction and pyrite flotation products were low.

To summarize, it can be concluded that rare metals Mo, U and V were concentrating in OM, their recovery in pyrite and quartz was negligible, depending on the degree of pyrite separation. The recovery of rare metals, especially that of V in the mineral phase, was more considerable in the processing of Maardu argillite, whose content of clay minerals was higher than that of Toolse argillite.

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РАСПРЕДЕЛЕНИЕ НЕКОТОРЫХ РЕДКИХ МЕТАЛЛОВ В ПРОЦЕССЕ ОБОГАЩЕНИЯ ЭСТОНСКИХ ДИКТИОНЕМОВЫХ АРГИЛЛИТОВ

Резюме

В наших предыдущих статьях [1, 2] были представлены схемы обогащения диктионемовых аргиллитов месторождений Маарду и Тоолсе в отношении органического вещества (ОВ) и пирита. В данной статье приведены данные о распределении модибдена, урана и ванадия в указанных процессах (рисунки 1 и 2; таблицы 1 и 2).

По использованной схеме измельченный аргиллит подвергали гидроциклонированию, слив направляли в процесс флотации ОВ, а пески — для выделения пирита. Полученные данные показывают, что в слив извлекалось 70—75 % редких металлов. Далее, в процессе флотации выделяли концентрат ОВ. В случае маардуского аргиллита в концентрат ОВ извлекались соответственно 46,4 % Mo, 46,4 % U и 28,5 % V, а в отходы после гидроциклонирования — соответственно 9,9, 19,7 и 35,1 %.

В процессе флотации слива от гидроциклонирования тоолсеского аргиллита выделяли концентрат с содержанием ОВ 61,5 %. Концентрации Mo, U и V в концентрате значительно превышали их исходные содержания: соответственно в 2,2, 2,0 и 1,6 раза. Но извлечение металлов в концентрат было небольшим — 24 — 34 % (извлечение ОВ 45,7 %), так как промпродукты в перечистке концентрата не возвращались обратно в процесс, а использовались для анализов. В отход флотации извлекалось 7—12 % редких металлов.

Пески гидроциклонирования направляли в процесс флотации пирита. Но в пиритовых фракциях (выход 30 %) содержания и извлечения Mo, U и V были небольшими, (в случае тоолсеского агриллита 4,6—7,4 %) и несущественными для выделения металлов.

Результаты анализов металлов показывают, что при обогащении тоолсеского аргиллита суммарное извлечение Mo, U и V в отходы, поступающие в отвалы и в пиритовые концентраты, составляло 22—25 %.

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