

**R. PALVADRE, B. NAUMOV, V. AHELIK,
I. LILLE, K. AGURAIUJA**

THE LEACHING OF DICTYONEMA ARGILLITES IN THE DUMPS OF PHOSPHORITE OPEN CAST MINING AT MAARDU

During the open-cast mining of phosphorite at Maardu, the Dictyonema argillites overlying the former were disposed of in dumps, their amount reaching about 24.1 million m³ [1]. Maardu Dictyonema argillites have a low organic content (~16 %) and a high content of sulfur (~4 %) and of rare metals. Of the latter, uranium (~40 g/t), molybdenum (~80 g/t) and vanadium (~470 g/t) are the most important, while titanium, copper, zinc, nickel and others are present in concentrations exceeding clarkes [2-4]. These unused argillites are a potential environmental hazard since they are prone to generate saline leachate and cause leaching of heavy metals into the water. They are also subject to self-ignition which leads to their thermal decomposition, which in turn promotes the leaching processes. In the quarry dumps the oxidation and decomposition of pyrite take place, causing a considerable discharge of sulfates into natural water and also increasing the leaching of heavy metals from argillite [5].

The leaching processes taking place at Maardu deposit have been investigated by several authors [6-8]. This paper aims at elucidating trends in the pollution level and at establishing its sources at Maardu phosphorite deposit after abandoning the open-cast in 1991.

The quarry water has come into being by atmospheric water movement through the vertical profile of the dumps, plus underground water and the water accumulated in the quarry trenches. The leaching process consists of water movement, resulting in chemical solute uptake and its subsequent transport within water. The argillites stored in different dumps have been affected differently in the course of years. Their layers have grown thicker which makes the penetration of water more difficult. On the other hand the cleavage of argillite particles facilitates the access of water and promotes thereby the leaching processes. Also, the dumps have been overgrown with vegetation which affects the filtration and evaporation of water. All these factors affect the leaching process of argillites. This paper presents results of analysis of the water samples taken in May 1992 in different parts of Maardu phosphorite deposit. The sampling points are shown in Figure. The analyses were carried out at the Institute of Chemistry of the Estonian Academy of Sciences. The analytical methods used are described in Table 1.

Hydrochemical and hydrogeochemical conditions differ in the northern and in the southern parts of the quarry. Slightly alkaline high-mineral (5.3-11.4 gL⁻¹) water containing magnesium and calcium sulfates characterises the northern area while low-mineral (1.1-2.4 gL⁻¹) water containing sodium and calcium sulfates as well as hydrocarbonates is typical of the southern area [8, 9]. The pumping station in the

Table 1. Analysis of the Water Samples

Sample No.	Components (in brackets method of analysis)							
	Zn (1)	Mn (1)	Cr (1)	Sn (1)	Cu (1)	Ni (1)	Pb (1)	Co (1)
1	0.59	0.59	0.041	—	0.021	0.17	0.050	—
2	0.24	0.16	0.028	0.14	0.036	0.23	0.014	—
3	0.12	0.29	0.013	—	—	0.11	0.014	—
4	0.10	0.27	0.084	—	—	—	0.035	—
5	0.13	0.11	0.013	—	—	0.09	—	—
6	0.87	0.93	—	—	—	0.35	0.014	0.04
7	2.54	1.33	—	—	—	0.86	0.014	0.11
8	0.14	2.16	0.057	—	—	0.18	0.014	0.04
9	1.07	1.36	0.028	—	—	0.41	—	0.08
10	0.67	1.26	0.013	—	—	0.39	—	0.10
11	0.17	0.08	—	0.79	—	—	—	—
12	0.87	1.01	0.013	0.33	—	0.32	—	—
13	0.77	0.46	—	0.33	—	0.22	—	—
14	0.17	0.64	—	0.47	—	—	—	—
15	1.40	1.10	0.084	0.79	0.008	0.31	—	0.04

Foot-note. Bars (—) indicate lower than detection limit. Analytical titration; 4 - ion chromatography.

northern part of the quarry (Point 13) is no longer working and the open-pit water is being discharged by way of underground excavation (Point 15) and via drainage trenches (Point 14) into the stream of Kroodi which is also the recipient of the treated industrial waste water of the Estonian Phosphorite Association and sewage of the town of Maardu.

Around the southern area a conical depression of underground water has come into being through the pumping of quarry water into Lake Maardu (Point 9). As a result, the underground water in the southern quarry flows southward [8, 9].

The four first water samples were taken from the Kroodi stream. The sample taken at the lower course of the stream (Point 1) shows the pollution load from Maardu deposit on the Gulf of Finland. The data presented in Table 1 show this water to contain very high concentrations of SO_4^{2-} , Cl^- , NO_3^- and F^- , and to be highly mineral as well [12]. The increased F^- content is probably due to the floto waste accumulated near the Kroodi stream. Data about the SO_4^{2-} content of water

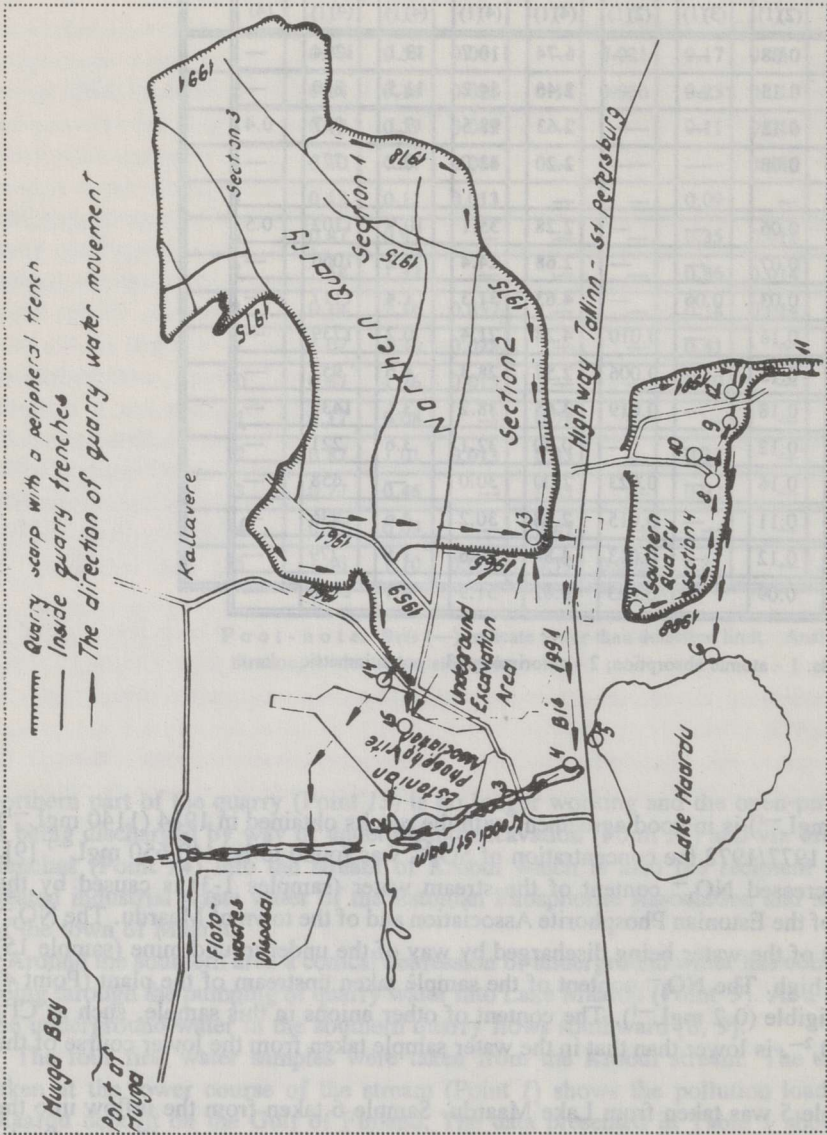
from Maardu Phosphorite Deposit

is indicated; for legend see the footnote)								
Fe (1)	Mo (2)	V (3)	U (2)	F ⁻ (4)	Cl ⁻ (4)	NO ₃ ⁻ (4)	SO ₄ ²⁻ (4)	PO ₄ ³⁻ (4)
3.64	0.08	—	—	6.74	110.7	13.1	1264	—
0.71	0.13	—	—	2.46	54.2	11.5	880	—
1.74	0.13	—	—	2.63	98.5	7.1	947	0.4
11.78	0.08	—	—	2.20	42.0	0.2	771	—
2.14	0.06	—	—	2.28	35.1	10.9	1102	0.5
0.79	0.07	—	—	2.68	24.4	5.2	1066	—
0.57	0.03	0.06	—	4.63	31.3	1.4	1117	—
6.71	0.16	—	0.010	4.28	21.4	0.2	1739	—
6.07	0.13	—	0.006	2.57	28.3	4.6	953	—
4.64	0.18	—	0.019	3.65	38.2	3.1	1438	—
2.43	0.12	—	—	0.80	32.1	3.6	221	—
4.66	0.16	—	0.023	2.00	30.0	—	658	—
0.36	0.11	—	0.015	2.08	30.2	4.6	1936	—
1.74	0.12	—	0.013	4.80	49.6	1.5	779	—
9.14	0.09	—	0.023	6.62	51.9	6.1	2608	—

methods: 1 - atomic absorption; 2 - colorimetry; 3 - potentiometric

(1260 mgL⁻¹) is in good agreement with the results obtained in 1984 (1140 mgL⁻¹) [1]. In 1977/1978 the concentration of SO₄²⁻ was found to be 440-650 mgL⁻¹ [9]. The increased NO₃⁻ content of the stream water (samples 1-3) is caused by the waste of the Estonian Phosphorite Association and of the town of Maardu. The NO₃⁻ content of the water being discharged by way of the underground mine (sample 15) is also high. The NO₃⁻ content of the sample taken upstream of the plant (Point 4) is negligible (0.2 mgL⁻¹). The content of other anions in this sample, such as Cl⁻ and SO₄²⁻, is lower than that in the water sample taken from the lower course of the stream.

Sample 5 was taken from Lake Maardu. Sample 6 taken from the inflow into the lake shows the pollution load on the lake from the southern quarry (Section 4). As can be seen, the concentration of heavy metals (Zn, Mn, Ni) in the inflow water that has been subjected to leaching, is considerably higher than the natural level (sample 5). On the other hand, the concentration of some components (NO₃⁻, Cl⁻) is higher

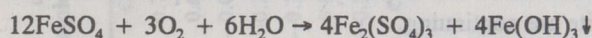
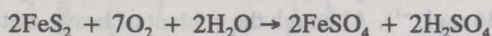


Map of Maardu phosphorite deposit (circles mark sampling sites, years indicate the time of excavation)

in the lake water than in the inflow, which indicates their origin from agricultural or industrial pollution while their content in the quarry water (samples 7, 8) is low. The concentration of sulfate ions in the lake water is very high, 1100 mgL^{-1} . It was approximately the same in [8], and was found to be $200\text{-}300 \text{ mgL}^{-1}$ [9] and $210\text{-}320 \text{ mgL}^{-1}$ [10] in 1977/1978.

Samples 7-12 were taken in the southern part of the quarry (Section 4). The high concentration of metals Mo, U, Zn, Mn, Ni, Co and Fe, as well as anions SO_4^{2-} and F^- is the common feature of all these samples, except the 11th one. Sample 7 was taken from the western part of the southern quarry (excavation in 1988) where the argillites lying on the surface of the dump have undergone cleavage. This water contains almost all the metals leached out from argillite, such as Zn, Mn, Ni, Co, V, as well as anions F^- and SO_4^{2-} . Water samples 9 and 12 were taken from that part of the quarry which was exploited most recently (1990).

Sampling Point 9 is located at the pumping station discharging the quarry water from the southern part into Lake Maardu. The quarry water flows from Sampling Point 7 towards Points 8 and 9. An increase of the metal content of samples, especially that of Mo, U and Fe, can be observed on this direction. The total content of heavy metals in samples from 7-9 increases from 5.68 to 9.35 mgL^{-1} . Since the quarry water from the eastern trench flows towards Point 12, the metal concentration in the appropriate sample is high. The concentration of rare metals Mo and U in quarry water is $0.13\text{-}0.18$ and $0.006\text{-}0.23 \text{ mgL}^{-1}$, respectively. The concentration of iron and sulfate ions is also high in all these water samples (Points 8, 9, 12). Iron hydroxide precipitates on the bottom of the trench, being in a colloidal state in the trench water. In the dumps oxidation and decomposition of pyrite take place:



The precipitation of iron hydroxide is accompanied by the co-precipitation of heavy metals.

Table 2. The Abundance of Metals in the Quarry Bottom Sediment (g/t)
(in brackets the metals contents of the argillite from southern part of Maardu deposit are indicated [4])

Mn	376 (200-400)	Pb	38 (30-70)
Cr	346 (40-70)	Co	23 (10-15)
Sn	184 (3-30)	Ni	87 (40-80)
Cu	220 (50-70)	Mo	30 (2-10)
Zn	1,200 (40-5,000)	V	92 (200-700)
Fe	103,000 (30,000-50,000)	U	57 (13-39)

In Table 2 the results of analysis of the open-pit bottom sediment from Point 12 are presented. The main component of this sediment is iron ($\sim 10\%$). The concentration of such metals as Pb, Cu, Ni, Sn, V, Cr, and Mn, is very high, while that of several sparingly soluble metals (V, Pb, Sn) in trench water is lower than the detection limit. The concentration of several metals in the bottom sediment is the same as in argillite, but the concentration of Cr, Sn, Cu and Zn is considerably higher in the bottom sediment.

Sample 11 was taken from trench water in the southernmost part of the quarry where limestone has been excavated only down to the glauconitic sandstone layer. Consequently there is no argillite leaching in this region, which accounts for the low contents of metals, and of anions SO_4^{2-} and F^- of this sample (some metals, such as Fe, and, to a lesser extent, anions SO_4^{2-} and F^- , may be leached out from glauconite, too). This indicates that metals and anions F^- and SO_4^{2-} in the quarry water originate from the leaching processes of argillite and from the decomposition of pyrite.

The SO_4^{2-} content of the quarry water sample taken from the pumping station (Point 9) has roughly doubled compared to 1977/1978 and 1984 when it was 450-800 [9] and 600 mgL^{-1} [1] respectively. The concentration values of Mo, V and U in the trench water are approximately the same as those determined in the studies of 1977/1978 (Mo 0.07 [10] and 0.12-0.21 [9] mgL^{-1} , V 0.008 [10] and 0.01 [9] mgL^{-1} , and U 0.009 [10] mgL^{-1}). For comparison, the average content of Mo in the river water is 0.001 mgL^{-1} [11]. The toxicological limit allowed for fish-breeding is 0.0004 mgL^{-1} [12].

Sample 13 was taken in the southern part of the northern quarry. This site is an old quarry (1965) where the dump surface is covered with vegetation and where no precipitation of colloidal iron hydroxide takes place. This is also borne out by the low iron concentration in water (0.36 mgL^{-1}). Although the content of heavy metals is lower than in the water from the southern quarry, the leaching process of argillites and decomposition of pyrite are continuing.

Sample 14 was taken in the northern part of Maardu deposit. The metal content of this water sample is lower than in the water sample from the southern quarry. It is almost the same as of sample 13, the content of Zn and SO_4^{2-} being low.

Table 3. Comparison of Contents of Water from the Northern and Southern Parts of the Quarry (Points 9 and 15)

	Removal of soluble components, $\text{t/10}^6\text{m}^3\text{y}$	Concentration, mgL^{-1}					Total content of heavy metals, mgL^{-1}
		SO_4^{2-}	NO_3^-	F^-	Cl^-	$\text{Fe}^{2+,3+}$	
Northern part (Point 15)	1,010	2,608	6.1	6.62	51.9	9.14	13.04
Southern part (Point 9)	656	953	4.6	2.57	28.3	6.07	9.35
Relationship	1.5	2.7	1.3	2.6	1.8	1.5	1.4

Table 4. The Correlation Matrix for Components of Water Samples from Maardu Phosphorite Deposit

	Mn	Cr	Sn	Cu	Ni	Pb	Co	Fe	Mo	V	U	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	PO ₄ ³⁻
Zn	0.44	-0.10	0.01	-0.11	0.92	-0.11	0.70	-0.10	-0.43	0.78	0.18	0.36	-0.21	-0.18	0.31	-0.32
Mn		0.19	-0.21	-0.28	0.54	-0.12	0.69	0.28	0.27	0.25	0.42	0.41	-0.37	-0.48	0.43	-0.40
		Cr	0.03	0.22	-0.20	0.41	-0.06	0.88	-0.02	-0.24	0.13	0.40	0.16	-0.01	0.44	-0.16
			Sn	-0.02	-0.27	-0.46	-0.29	0.06	0.10	-0.18	0.44	0.03	-0.11	-0.14	0.11	-0.27
				Cu	-0.04	0.41	-0.25	-0.15	-0.01	-0.12	-0.22	0.26	0.46	0.68	0.04	-0.17
					Ni	-0.11	0.82	-0.19	-0.25	0.77	0.11	0.24	-0.26	-0.16	0.24	-0.26
						Pb	-0.19	0.21	-0.34	0.07	-0.52	0.35	0.59	0.30	-0.08	-0.11
							Co	0.06	-0.03	0.58	0.14	0.26	-0.35	-0.30	0.25	-0.28
								Fe	0.14	-0.26	0.28	0.20	-0.06	-0.33	0.25	-0.22
									Mo	-0.53	0.53	-0.21	-0.08	-0.26	-0.04	-0.18
										V	-0.22	0.20	-0.15	-0.23	-0.02	-0.10
											U	0.24	-0.25	-0.40	0.50	-0.32
												F ⁻	0.44	0.19	0.59	-0.22
													Cl ⁻	0.60	0.01	0.28
														NO ₃ ⁻	0.10	0.41
															SO ₄ ²⁻	-0.09
																PO ₄ ³⁻

Sample 15 was taken in the grounds of the Estonian Phosphorite Association. This water originates mainly from the old underground phosphorite mine. The concentration of such metals as Zn, Mn, Cr, Sn, Ni, and especially Fe, as well as of anions F^- , Cl^- , NO_3^- and SO_4^{2-} , is very high. These components originate from argillite leaching, as well as from the industrial waste and sewage of the Kallavere region.

Calculations [1, 8] show that the amounts of soluble components removed from argillites by water are different in the northern and in the southern parts of the quarry. The results of an analysis of water samples from the northern and from the southern parts of the quarry (Points 15 and 9; Table 3) show that water from the northern part has a higher mineral content, that of metals being higher by a factor of about 1.4. According to several authors [8, 9] a considerable release of components from argillite in the northern area of the quarry is caused by its self-ignition and combustion. But, as mentioned above, several components in the water from the northern quarry probably originate from industrial and communal waste.

The data presented in the Table 4 show that there is a positive correlation between U and Mo. These metals tend to be leached out from argillite as demonstrated by lab tests [7]. Uranium is correlated with SO_4^{2-} , which shows that it is leached in the form of a soluble uranyl sulfate complex $[UO_2(SO_4)_2]^{2-}$. Zn, Ni, Co and Mn are positively correlated with each other. All of them are derived from the leaching processes of argillites and of glauconitic sandstone and their concentration in the quarry water is higher than that of sparingly soluble heavy metals, such as Pb and Sn. There is a weak correlation ($r=0.25$) between Fe and SO_4^{2-} although they are both mainly derived from the oxidation and decomposition of pyrite. But, as mentioned above, Fe has precipitated as hydroxide due to hydrolysis of the products of decomposition of pyrite. In addition, Fe, as well as Cr, Cu and Pb, originate partly from industrial waste (samples 4 and 15). The presence of the ions NO_3^- and Cl^- is not due to the leaching processes of argillites, and they have a negative correlation with metals and with SO_4^{2-} ions, with the exception of Cu and Pb which also originate mainly from industrial waste.

Conclusions

An assessment of the ecological state of the Maardu phosphorite open-cast mining area, as well as of the pollution load on the Gulf of Finland and on Lake Maardu from Maardu quarry, is presented. These investigations show that leaching processes of argillites have been continuing in the quarry dumps after abandoning the phosphorite open-cast. The high contents of sulfate and iron ions in quarry water indicate that oxidation and decomposition of pyrite are still taking place at present. The abundance of heavy metals in the red-brown ironiferous bottom sediment is indicative of their co-precipitation with iron hydroxide.

Acknowledgements

The authors wish to thank H. Tamvelius for correlation calculations and R. Sild for help with the preparation of the manuscript.

Р. ПАЛВАДРЕ, Б. НАУМОВ, В. АХЕЛИК, И. ЛИЛЛЕ, К. АГУРАЙУА

ВЫЩЕЛАЧИВАНИЕ ДИКТИОНЕМОВЫХ АРГИЛЛИТОВ В ОТВАЛАХ ФОСФОРИТНОГО КАРЬЕРА МААРДУ

Резюме

Определено содержание тяжелых металлов и анионов в водах пространства Маардуских карьеров (рисунок). Цель — оценить, в какой степени продолжается выщелачивание диктионемового аргиллита в отвалах и как это влияет на окружающую среду.

Анализы вод ручья, протекающего по оврагу Крооди (пробы 1—3, табл. 1), которые характеризуют нагрузку загрязнения, поступающего в Финский залив, показывают высокое содержание анионов SO_4^{2-} , Cl^- , NO_3^- и F^- . При этом высокие концентрации анионов NO_3^- и Cl^- могут быть объяснены поступлением в овраг Крооди промышленных и бытовых стоков г. Маарду после их очистки.

Карьерные воды (пробы 7—12 из Южного карьера и пробы 13—15 из Северного карьера, табл. 3) содержат много тяжелых металлов и сульфата. В результате окислирования и разложения пирита в воде Южного карьера там наблюдается интенсивное осаждение гидроокиси железа и вместе с этим соосаждение тяжелых металлов (таблицы 2 и 4). О выносе элементов с карьерными водами из Южного карьера в озеро Маарду можно судить по пробе 6 (табл. 1).

REFERENCES

1. Naumov B. Pollution of hydrosphere by leaching of *Dictyonema* shale in waste dumps of the Maardu openpits (Summary) // *Goryuchiye slantsy* (Oil Shale). 1991. Vol. 8, No 3. P. 273.
2. Pelekis L., Pelekis Z., Taure J., Kirret O., Rajavee E. Instrumental neutron activation analysis of alum shale from the Maardu deposit (Summary) // *Proc. Est. Acad. Sci., Chem.* 1985. Vol. 34, No 3. P. 164.
3. Pukkonen E. M. Major and minor elements in Estonian graptolite argillite (Summary). // *Goryuchiye slantsy* (Oil Shale). 1989. Vol. 6, No 1. P. 18.
4. Pihlak A., Izand D. Composition of the Maardu *Dictyonema* shale of Estonia and its tendency to self-ignition (Summary) // *Ibid.* No 3. P. 258.
5. Althausen M., Maremäe E., Johannes E., Lippmaa E. Weathering of metalliferous alum shales (Summary) // *Proc. Est. Acad. Sci., Chem.* 1980. Vol. 29, No 3. P. 169.
6. Pihlak A., Maremäe E., Jalakas L. Leaching processes of the alum shale and limestone from Maardu and Toolse phosphorite quarries (Estonian SSR) (Summary) // *Goryuchiye slantsy* (Oil Shale). 1985. Vol. 2, No 2. P. 169.
7. Palvadre R., Ahelik V., Rajavee E., Juga R. Some aspects of water leaching of argillites (Summary) // *Proc. Est. Acad. Sci., Chem.* 1990. Vol. 39, No 4. P. 241.
8. Naumov B., Karise V. Outflow of mineral substances from Maardu phosphorite openpit into the gulf of Finland (Summary) // *Ibid. Geol.* 1991. Vol. 40, No 4. P. 172.
9. Johannes E., Karise V., Punning J.-M., Hütt G. Hydrogeological and geochemical investigations of ecological state of Maardu phosphorite deposit (in Russian) // *The environmental pollution of North Estonia*. Tallinn, 1979. P. 88-102.
10. Maremäe E., Pihlak A., Lippmaa E. The self-ignition of *Dictyonema* shale and the leaching of heavy metals from products of its combustion (in Russian) // *Ibid.* P. 74-87.

11. J. E. Huheey. Inorganic Chemistry. - Moscow, 1987.
12. Water quality and water protection. Comp. by A. Saava. Refresher Courses for Leading Persons and Specialists of Estonian National Economy. - Tallinn, 1986 (in Estonian).

Presented by J. Kann

Received January 18, 1994

Estonian Academy of Sciences
Institute of Chemistry

Estonian Academy of Sciences
Institute of Geology

Tallinn, Estonia