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THE INFLUENCE OF THE URBAN ENVIRONMENT ON THE STONE OF THE ARENA IN PULA

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Key-words: Dimension stone, Decay, Vinkuran quarry, Arena in Pula, Sulphates, Chlorides, Heavy metals

The paper presents data on quantity of sulphate, chloride and metals in stone samples from the Vinkuran quarry and stone blocks from the external curved wall of the Arena in Pula. It has benn established that the stone from the Vinkuran quarry contains insignificant content of primary soluble salts (sulphates and chlorides) and parts of metal. A considerable increase in concentration of sulphates (to 92 times), as well as chlorides and metals, particularly lead (to 36 times), has been noticed in the surface layer of stone from the external curved wall of the Arena.

Ključne riječi: Arhitektonski kamen, Trošenje, Kamenolom Vinkuran, Arena u Puli, Sulfati, Kloridi, Teški metali

Izloženi su podaci o količini sulfata, klorida i metala u uzorcima kamena iz kamenoloma Vinkuran i kamenih elemenata vanjskog plašta Arene u Puli. Utvrđeno je da kamen iz kamenoloma Vinkuran sadrži neznatne količine topivih soli i metala. Značajno povećanje sulfata (do 92 puta), kao i klorida i metala, posebice olova (do 36 puta), dokazano je u površinskom dijelu kamena vanjskog plašta Arene.

Introduction

The external curved stone wall of the Arena in Pula has been built of limestone blocks originating from the ancient »Cava Romana«, at present Vinkuran quarry, in the vicinity of Pula. To the west of Vinkuran there is an abandened ancient quarry and an ancient where even nowadays blocks of dimension stone are quarried (Crnković, 1988, 1991).

At the First International Conference »*The Three Arenas: Pula, Verona, Rome*«, held in Pula 1988, the dicsussion on the protection of the amphitheatre touched on felicitous circumstances that there is no industry in Pula which would more seriously pollute the urban environment. The stone of the amphitheatre was threatened, however, by influence of »acide rains« and urban traffic. Some 30 years ago several samples were taken from the surface layer of the stone blocks in the outer curved wall of the Arena, in which qualitative reaction on sulphate ion (by means of barium chloride) was negative, and the reaction on chloride ion (by means of silver nitrate) was positive. A quantitative analysis of the samples was not carried out on at that occasion.

The influence of »acide rains« and other pollutants as a product of urban environment on the building stone can be determined best by comparing content of corresponding elements in the original stone from deposit with the stone used for building and exposed to the activity of exogenic, natural and technogenic factors. Samples of stone from the »Cava Romana« (Vinkuran) quarry were analyzed for that purpose as well as samples of the stone from the outer curved wall of the Arena.

Testing methods

Samples were taken from the Vinkuran quarry along a vertical profile from beds approximately 1.2 m thick (Fig. 1). The total of 10 samples comprises »unito« and »fiorito« stone types.

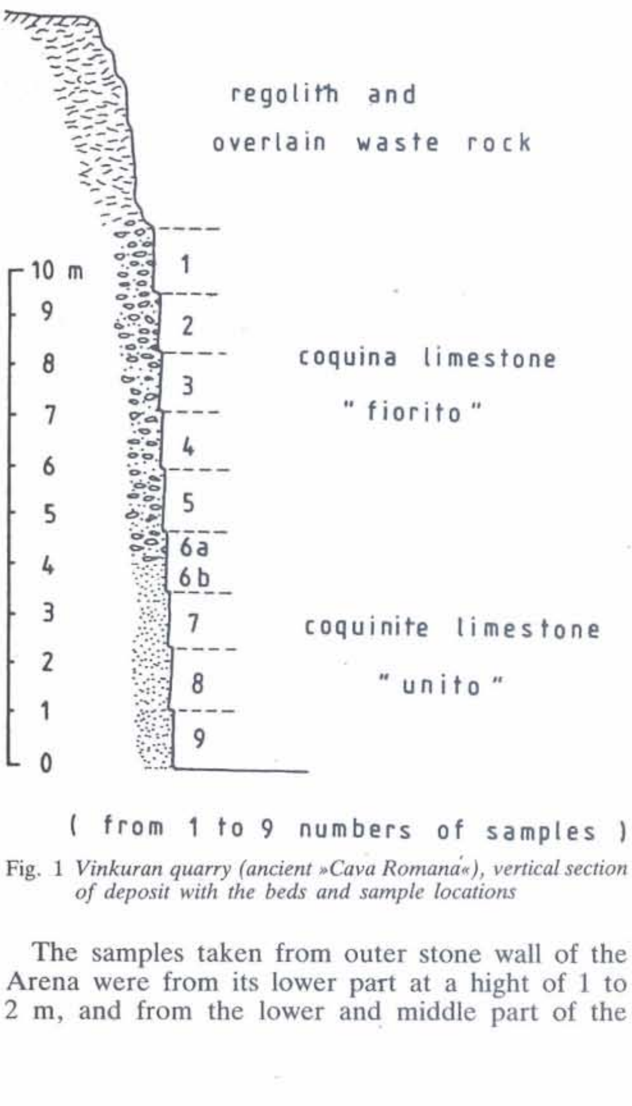

Fig. 1 *Vinkuran quarry (ancient »Cava Romana«), vertical section of deposit with the beds and sample locations*

The samples taken from outer stone wall of the Arena were from its lower part at a hight of 1 to 2 m, and from the lower and middle part of the

Table 1
Location of the stone samples from the curved wall of the Arena (fig. 2)

mark	location of sample
1	western part of Arena, lowest part of curved wall near the road at a hight of 0.5 m, sample broken off along a crack of surface disintegration
2	northwestern part of Arena, lower part of tower, sample from a broken off shell with black patina, up to 0.5 mm thick
3	northwestern part of Arena, middle part of the tower, sample of black patina and crust from a stone arch
4	northwestern part of Arena, sample taken from the tower crenel, stone surface with grey patina and »karstification«, stone type »unito«
5	northern part of Arena, crust separated at 1.5 m above ground
6a	eastern part of Arena, separated and disintegrated stone surface with grey patina and »karstification«, stone type »unito«
6b	eastern part of Arena, sample taken from thick separated stone plate
6c	eastern part of Arena, sample from a block with grey patina
6d	eastern part of Arena, sample of black patina and approximately 2 mm thin crust
7	southeastern part of Arena, sample taken from stone with platty disintegration on the surface
8	southern part of Arena, sample taken from a block with plate disintegration on the surface
9	southern part of Arena, sample of stone with black patina and crust, taken underneath an arch

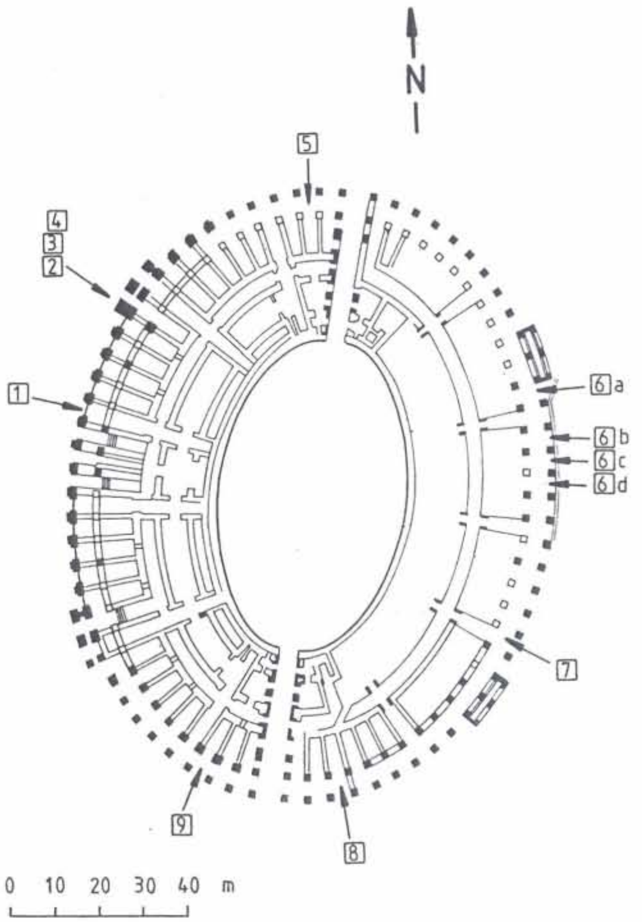

Fig. 2 *Stone wall of the Arena in Pula, with the sample locations*

tower (Fig. 2). The total of 12 samples were taken from the surface stone blocks in places of conspicuous surface damage and from parts with black patina and crusts (Table 1). A part of the samples was examined by microscopy.

To determine presence of sulphate and chloride ion a sample of approximately 5 g of crushed stone from the deposit was taken and 2.5 g of crushed stone from the outer curved wall of the Arena. After drying the samples at temperature of 110°C and weighing, the powder was then digested in boiled distilled water. In the filtrates obtained after dissolution in water and filtering, sulphate ions were determined by gravimetry as barium sulphate, and chloride ions by the Mohr method.

Apart from the anions mentioned the content of some heavy metals in the samples was also determined like: mercury, cooper, nickel, cobalt, zinc, lead and cadmium.

The content of mercury was determined directly from the powdered samples by means of the standard mercury analyzer with sensitivity $20x10^{-9}$ mg/m^3 in air or gas (Palinkaš et al. 1990).

Other metals were determined by atomic absorption spectrophotometry (AAS). The samples were prepared as follows: 2 g of powdered limestone was treated by 2 M hydrochloric acid solution »drop by drop« and digested. This was done to prevent leaching of trace elements from insoluble clay fraction of the limenstones. The solution of the decomposed sample was then dilluted to 50 cm^3 volume with deionized water. Matrix of the standard solutions for each element was matched by calcium carbonate and hydrochloric acid to the concentrations of the sample solutions.

Description of the deposit

The Vinkuran quarry is situated in rudist limestone of the Upper Cretaceous age (Turonian), studied and described in detail by Tišljar (1976). They are biostromal »coquina« and »coquinite« limestones of similar texture.

The »*couquina*« limestone is mostly of poorly sorted, sometimes very large shells and shell debris of rudists. The limestone is in market designated as the »fiorito« type because of its large rudist remnants in calcite matrix. Since it is medium to poorly cemented, it is sometimes characterized by great porosity and conspicuous voids, so it is also known under commercial name »travertino«.

»*Coquinite*« is a limestone built from well sorted and mechanically reworked tiny debris of rudist skeletons in fine crystalline calcite matrix. In market it is designated as the »unito« or »statuario« type.

The »coquinite« lies at the bottom part of the deposit, and the »coquina« at the top (Fig. 1).

Either limestone types are rocks with high calcite content, approximately 99% $CaCO_3$. The insoluble residue contains illite and kaolinite in abundance, and only insignificant amounts of quartz, albite, goethite, hematite, boehmite, hydromica, anatase and apatite.

The textural features of both limestone types described reflect their physical and mechanical properties, which are presented in Table 2.

Table 2
Physical and mechanical properties of »unito« and »fiorito« limestone types from the Vinkuran quarry

property	»fiorito«	»unito«
Compressive strength (MN m^{-2})		
dry samples	36.5	58.5
water-saturated samples	32.5	57.0
after freezing and thawing	29.0	49.0
Bending strength (MN m^{-2})	3.3	10.1
Density (kg m^{-3})	2708	2711
Bulk density (kg m^{-3})	2251	2272
Porosity (vol. %)	16.9	16.2
Water absorption (mas. %)	5,52	6.02
Longitudinal wave velocity (km sec^{-1})		
dry samples	3460	4416
water-saturated samples	3354	4293

Properties determined by Građevinski institut (Institute of Civil Engineering), Zagreb.

As it be established visually, both limestone types, »unito« and »fiorito«, are built into the outer curved wall of the Arena.

Gypsum in the stone of the outer curved wall of the Arena

Four samples of stone from the outer curved wall of the Arena (samples A-2, A-3, A-5 and A-9. Fig. 2), characterized by increased sulphate ion content, were examined by microscopic analysis.

It was determined that gypsum is found in fine fibrous and tabular forms as follows:

- in fine intergranular and interskeleton pore space,
- in more conspicuous oval and irregular cavities,
- in the black semi-opaque and opaque patina on the stone surface,
- resembling to a thin crust on the surface of the stone with fine tabular crystals, unoriented (Fig. 3a), and
- along fine cracks, resembling to thin veins with elongated crystals directed vertically to wall of cracks (Fig. 3b).

Sulphates and chlorides in the stone of deposit and in the outer curved wall of the Arena

Quantities of sulphate and chloride found in the stone of deposit and in the outer wall of the Arena are presented in Tables 3 and 4, and in Fig. 4.

Detectable quantities of sulphate were established only in two samples of stone from the upper part of the deposit, and chloride only in five samples from the lower part.

The arithmetic mean of sulphate quantity in the deposit stone was 0.02%, and of chloride 0.01%, which corresponds to the quantity of primary soluble salts determined in Cretaceous limestone rocks quarried for dimension stone in Croatia (Crnković and Babić, 1983).

The increase of chloride in the stone of the outer wall of the Arena and insignificantly more chloride in samples on the southwestern, western and northwestern parts of the outer wall, i.e. in those parts that are nearer to the coastline has been caused by vicinity of the sea. The stone of the tower does not

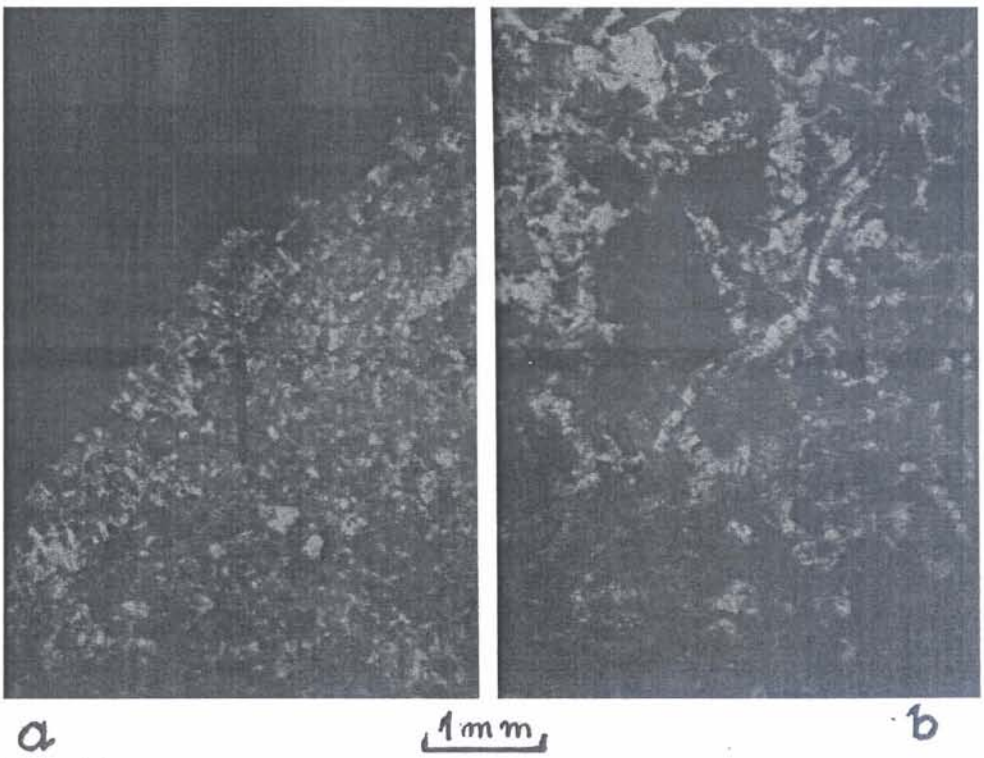

Fig. 3 Sample: A-9
a – unoriented fine tabular crystals of gypsum in thin crust on the surface of stone, marked with arrow, +N
b – elongated crystals of gypsum in the thin vein, filling of fine crack, marked with arrow, +N

Table 3
Quantities of sulphate and gypsum in the stone of deposits (Vinkuran quarry, fig. 1) *and in the outer curved wall of the Arena* (fig. 2, and table 1) *in %*

sample	SO_4^{--}	$CaSO_4 \cdot 2H_2O$
quarry		
K-1	0.09	0.15
K-2	0.09	0.22
K-3 to K-9	0.00	0.00
	0.00	0.00
Arena		
A-1	0.31	0.55
A-2	2.29	4.05
A-3	2.54	4.55
A-4	0.07	0.13
A-5	2.44	4.38
A-6a	0.19	0.32
A-6b	0.19	0.35
A-6c	0.20	0.36
A-6d	4.66	8.35
A-7	1.51	2.71
A-8	1.94	3.37
A-9	5.57	9.98

Table 4
Quantities of chloride in the stone of deposits and in the wall of the Arena in %

sample	Cl^-
quarry	
K-1 to K-5	0.00
	0.00
K-6a	0.03
K-6b	0.02
K-7	0.02
K-8	0.03
K-9	0.04
Arena	
A-1	0.11
A-2	0.23
A-3	0.15
A-4	0.04
A-5	0.06
A-6a	0.04
A-6b	0.04
A-6c	0.04
A-6d	0.08
A-7	0.04
A-8	0.06
A-9	0.06

contain such a quantity of chloride. This is loghical, since the chlorides, as easily soluble salts are readily wash out by rain water after their introduction into the pore space of the stone.

It is certain that sulphate contained in the outer wall of the Arena, particularly in the black patina and crusts on the parts protected from rains, derives from »acide rains« enriched in sulphuric acid and by traffic pollution.

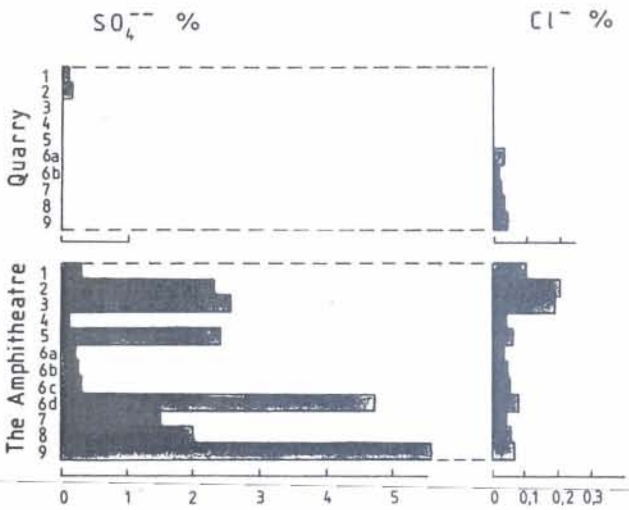

Fig. 4 *Frequency distribution of sulphate and chloride in the stone of deposit (quarry) and in the outer wall of the Arena (Amphiteatre), in percentages*

Heavy metals in the stone of deposit and in the outer curved wall of the Arena

Quantities of mercury, cooper, cobalt, nickel, zink and lead in the stone of deposit and the outer wall of the Arena are presented in Table 5 and Figs. 5, 6, 7 and 8. Table 6 shows the arithmetic means of the metal content in the stone of deposit and the Arena stone. Cadmium shows no increase in the stone of the Arena by antropogenic influence.

Comparing the arithmetic means of metal quantities in the stone of the deposit and the Arena, we

Table 5
Quantities of metals in the stone of deposits and in the wall of the Arena (Hg in ppb, other metals in ppm)

sample	Hg	Cu	Ni	Co	Zn	Pb
quarry						
K-1	5	0.4	4	1	2.3	~1
K-2	4	0.7	4	1	1.8	~1
K-3	9	0.2	2	1	2.5	~1
K-4	3	0.9	6	1	2.1	~1
K-5	3	0.8	3	1	1.8	~1
K-6a	2	3.9	8	2	1.8	~1
K-6b	4	0.8	4	2	1.9	~1
K-7	2	1.1	6	1	1.5	~1
K-8	4	0.4	2	2	2.0	~1
K-9	2	0.7	4	1	2.0	~1
Arena						
A-1	5	1.4	9	2	6.6	22
A-2	4	3.9	14	2	17.7	13
A-3	36	3.6	18	2	37.5	250
A-4	4	1.1	15	2	8.0	1
A-5	8	3.0	4	2	12.5	11
A-6a	8	2.7	11	1	5.9	3
A-6b	28	1.8	9	2	8.2	4
A-6c	8	1.0	13	2	10.2	4
A-6d	24	5.0	18	3	33.0	25
A-7	15	2.9	12	2	16.4	81
A-8	10	2.9	4	1	8.0	3
A-9	21	6.1	11	3	30.7	18

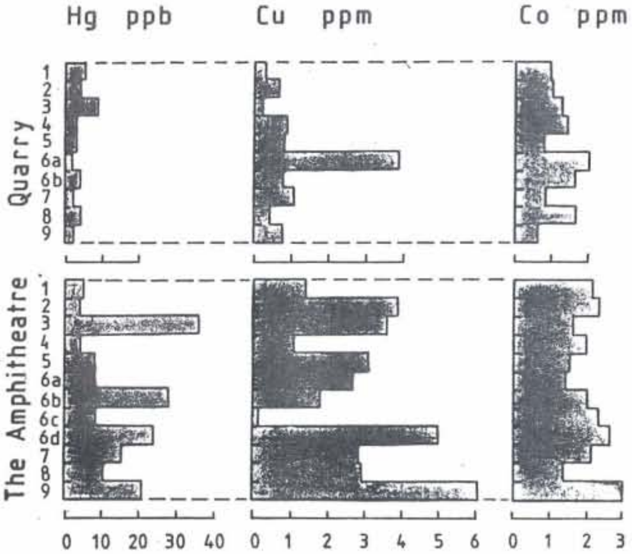

Fig. 5 *Frequency distribution of mercury (in ppb) and copper and cobalt (in ppm) in the stone of deposit and in the outer wall of the Arena*

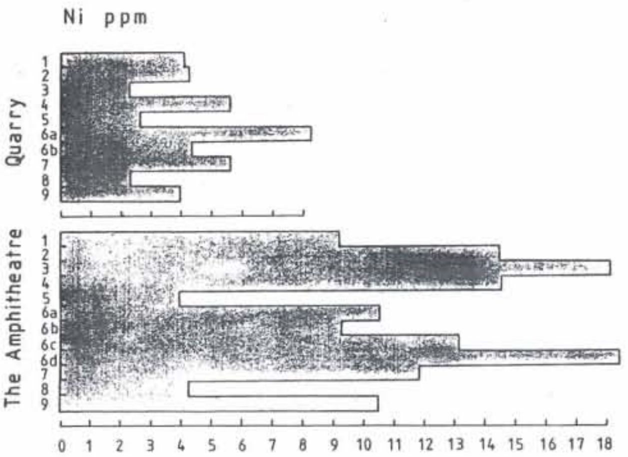

Fig. 6 *Frequency distribution of nickel (in ppm) in the stone of deposit and in the outer wall of the Arena*

Table 6
Arithmetical mean of metal quantities in the stone of deposit and in the wall of the Arena

metal	arithmetical mean		enlarged
	quarry	Arena	
Hg (ppb)	3.8	14.2	3.5 times
Cu (ppm)	0.9	2.9	3.3 times
Ni (ppm)	4.3	11.5	2.7 times
Co (ppm)	1.0	2.0	2.0 times
Zn (ppm)	2.0	16.2	8.0 times
Pb (ppm)	1.0	36.2	36.2 times

can notice insignificantly small increase of some metals, for instance cobalt (only 2 times), cooper and nickel, and very significant increase of zink (8 times) and lead particularly (36 times).

Discussion

The characteristic of the stone of deposit that contains insignificant content of primary soluble salts, chlorides and sulphates. Small quantity of sulphate was determined at the top of the deposit, in the limestone of the »fiorito« type. Small quantity of chloride was determined at the bottom part of the deposit, primarily in the »unito« limestone type.

A significant increase of sulphate was determined in the stone of some parts of the outer curved wall of the Arena. The maximum increase of sulphate was determined in samples of black patina, and crust from the stone surface layer. Quantity of sulphate, expresses as gypsum in samples A-6d and A-9 makes 8.35% and 9.98%. In sample A-9 the gypsum has been microscopically determined, both in the surface part of the patina, and in the fine cracks that cut across the limestone like thin »veins«.

Content of chloride is considerably lower than that of sulphate, with logical chloride increase in the stone of the Arena nearest to the coastline.

Heavy metals analysis in the stone of deposit is interesting from geochemical point of view and genesis of organogenic sediments. We shall not discuss this matter since, it lies outside our present concern, but we shall lay stress primarily on the possible origin and source of metals contributing to their pronounced increase in the outer curved wall of the Arena. The sources of metals are various waste products in urban and industrial environment, in other words products of human activities. The concentration of mercury increases by fossil fuel combustion. Petrol still contains 0.15 to 1.3 g/l of lead. According to Tjutjunova (1987) the rainwater of urban and industrial environment contains: 0.00015–0.00066 mg/l Hg, 0.001–0.0112 mg/l Cu,

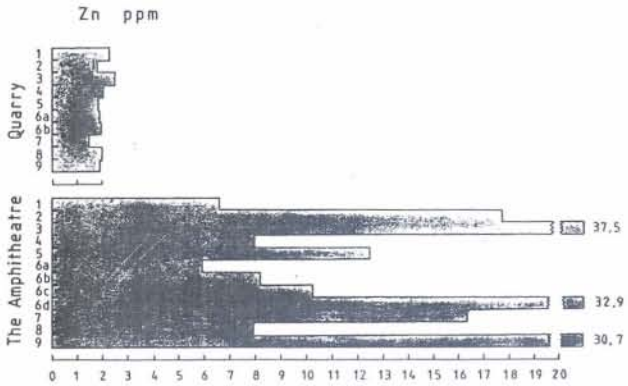

Fig. 7 *Frequency distribution of zink (in ppm) in the stone of deposit and in the outer wall of the Arena*

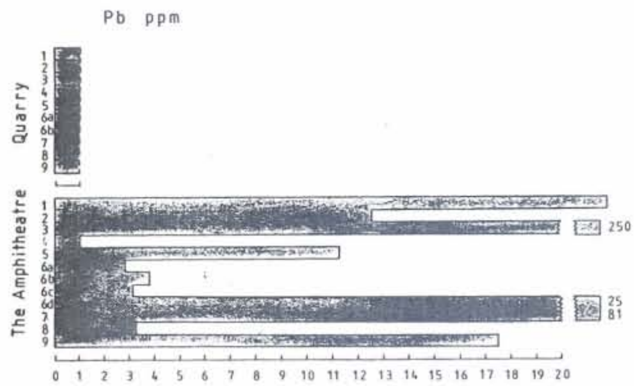

Fig. 8 *Frequency distribution of lead (in ppm) in the stone of deposit and in the outer wall of the Arena*

0.0006–0.073 mg/l Ni, 0.0003–0.0036 mg/l Co, 0.005–0.101 mg/l Zn, and 0.006–10.0 mg/l Pb.

All metals are contained in air as aerosol. Falling they settle on the stone surface layer, migrate and accumulate inside the stone.

The accumulation of some elements, for example lead, are enormous in some parts of the outer wall of the Arena. In relation to the stone of deposit, they are increased in the Arena wall 250 times (sample A-3).

Negative and harmful influence of calcium sulphate formation, anhydrite and gypsum, on the stone, i.e. limestone, under the effect of »acide rains« is well known and has been described elsewhere.

It is unknown, however, in what manner is the durability of dimension stone influenced by metals, and by changes of their compounds and transformations, accompanied by changes in volume, that are likely to occur.

For instance through petrol combustion lead tetramethyl and tetraethyl are introduced into the environment. Lead is contained in the aerosols in the form of halogenides and oxihalogenides, sulphates and phosphates, lead hydroxide and carbonate, as well as in complex compounds.

Lead is introduced by a posible substitution reaction in carbonate rocks:

$$CaCO_3 + Pb^{++} \rightarrow PbCO_3 + Ca^{++}$$

$$CaMg(CO_3)_2 + 2\,Pb^{++} \rightarrow 2\,PbCO_3 + Ca^{++} + Mg^{++}$$

All these possible processes and transformations, not only of lead but also of other metals, have not yet been fully studied nor sufficiently understood, so there is no ground for a discussion of their influence on the dimension stone.

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Utjecaj urbanog okoliša na kamen Arene u Puli

B. Crnković i S. Miko

Vanjski kameni plašt Arene u Puli izgrađen je od blokova i elemenata vapnenaca porijeklom iz antičke »Cava Romana«, danas aktivnog kamenoloma Vinkuran nedaleko Pule.

Utjecaj urbanog okoliša i »kiselih kiša« na kamen ugrađen u građevine najbolje se može utvrditi usporedbom odgovarajućih elemenata u kamenu iz kamenoloma i kamenu ugrađenom u objekte.

U kamenolomu Vinkuran duž vertikalnog profila uzeto je 10 uzoraka (sl. 1) kamena tipa »unito« i »fiorito«.

U kamenu plašta Arene u Puli uzeto je 12 uzoraka (sl. 2 i tablica 1).

U uzetim uzorcima analizirane su topive soli (kloridi i sulfati) i teški metali (Hg, Cu, Ni, Co, Zn, Pb i Cd).

Kamenolom Vinkuran se nalazi u rudistnim vapnencima gornje krede (turon), koje je detaljno obradio i opisao Tišljar (1976). U donjem dijelu ležišta prevladavaju »coquiniti« poznati kao tip »unito« ili »statuario«. U gornjem dijelu ležišta prevladavaju »coquina« vapnenci, poznati kao tip »fiorito« ili »travertino«. Oba tipa vapnenaca ugrađeni su u vanjski plašt Arene.

Četiri uzorka kamena plašta Arene, u kojima je utvrđen povećan udio sulfata, analizirana su mikroskopski. Utvrđeno je da se gips nalazi:

- u sitnom intergranularnom i interskeletalnom pornom prostoru,
- u nepravilnim šupljinama,
- u crnoj poluopâkoj i opâkoj patini na površini kamena,
- u tankim krastama na površini kamena (sl. 3a), i
- u sitnim prslinama poput žilica (sl. 3b).

Količine sulfata i klorida u kamenu iz ležišta i plašta Arene date su u tablicama 3 i 4. Količine sulfata i klorida u kamenu ležišta odgovaraju količinama topivih soli određenih u krednim vapnencima koji se u Hrvatskoj eksploatiraju kao arhitektonski kamen (Crnković i Babić, 1983).

Značajno povećanje klorida i posebno sulfata utvrđeno je u kamenu plašta Arene. Udio sulfata povećan je 92 puta, što je rezultat utjecaja »kiselih kiša« i gradskog prometa.

Količine teških metala (Hg, Cu, Co, Ni, Zn i Pb) u kamenu ležišta i vanjskog plašta Arene date su u tablici 5. Podaci za kadmij nisu dati, jer udio kadmija je približno jednak u kamenu iz ležišta i plašta Arene.

U tablici 6 prikazane su aritmetičke sredine udjela metala u kamenu ležišta i plašta Arene, kao i naznačeno njihovo povećanje u kamenu plašta Arene. Najznačajnije je povećanje olova, 36 puta.

Povećanje klorida u kamenu plašta Arene, iako neznatno, potječe od utjecaja mora.

Povećanje sulfata u kamenu plašta Arene, vrlo je značajno, potječe od utjecaja »kiselih kiša« i onečišćenog urbanog okoliša.

Negativno djelovanje i štetno djelovanje kalcijevog sulfata, anhidrita i gipsa, u vapnencima ugrađenim u objekte urbanih okoliša, dobro je poznato u literaturi i praksi.

Nije međutim poznato kako na trajnost vapnenca utječe povećanje udjela metala, transformacije njihovih spojeva, te vezano s time i odgovarajuće promjene volumena novonastalih tvorbi.