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Accumulation of moderate and highly soluble salts in soils: Implication for protection of underground steel structures in Slovakia

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Abstract: Underground structures, represented by the steel constructions buried in depth 80-250 cm in soil, are the most important technological systems for transfer of strategic media like natural gas and crude oil in Slovakia. Among the most important of them belong Transit gas pipe-line, International gas pipe-line "Bratstvo" and oil pipe line "Družba". Operation and protection costs for trouble free use of these structures reaches enormous prices yearly. The most damages are caused by the degradation of protective coatings and consequently by the corrosion of metallic body. One of important factors negatively influencing both the protective coatings and the steel body corrosion is the natural inorganic salt occurrence in saline soils.

Key words: underground structures, porous protective coatings, natural soluble inorganic salts, Danube and East Slovakian lowlands

Introduction

One of the most principal protection technologies of buried steel pipe-lines is the application of protective coatings that should in the ideal case perfectly isolate the steel body against the direct contact to rocks and soils as well as to included media chemistry – mainly to soil solutions.

Soluble inorganic salts like natron, thermonatrite, and gypsum were identified using XRD (X-ray powder diffraction) in the form of efflorescence on bituminous protective coating of the high-pressure gas pipeline from southern part of the Danube Lowland. Besides these minerals typical for saline soil there were identified also mostly common clay minerals, calcite, dolomite and quartz. Depending mainly on groundwater level changes dynamics and on local climatic changes, the dissolution and re-crystallization of moderately ($CaCO_3$, $CaSO_4$ x $2H_2O$) and highly soluble (sodium) salts could cause considerable degradation of porous protective coatings. Consequently, the corrosion of steel underground structures is accelerated. Such conditions, i.e. saline soil environment often combined with agrochemical pollution could be expected in the most arid and hottest lowland areas of East Slovakian and Danube lowlands.

Characteristic of saline soils and their impact to protective coatings

Saline soils originate in various environmental conditions, however mostly in arid to semiarid climatic regions. Such conditions occur in our country often in local non-effluent terrain depressions situated on transitions from alluvia to uplands. The most frequent anions associated with the saline soils are chlorides, sulphates, carbonates and nitrates, while sodium, potassium, calcium and magnesium represent the common cations. The accumulation of easily soluble inorganic salts is characteristic for saline soils (e.g. Na_2CO_3 x H_2O, Na_2CO_3 x $10H_2O$, $CaSO_x$ x $SrSO_4$, $CaSO_x$ x $2H_2O$, Na_2SO_4, $MgSO_4$, NACl, $MgCl_2$, $NaNO_3$) and their active participation in biological and geological cycle and migration. Based on the quantity and nature of contained salts the soils can be divided into three groups. This classification depends on total amount of dissolved salts expressed by their electric conductivity, soil pH value and percentage of exchangeable natrium (Szabolcz, 1991):

Soil classification	El. conductivity [mS/cm]	pH of soil	% of exchangeable Na
Saline	> 4.0	< 8.5	< 15
Sodic	< 4.0	> 8.5	> 15
Salsodic	> 4.0	< 8.5	> 15

Corrosion processes running on the surface of metallic body in contact with various types of environments cause a continual degradation of material due to chemical and/or physical-chemical effects. Corrosion processes have various character in various environments, and that it is important to define in detail factors mostly influencing the corrosion.

Potential risk of degradation of bituminous protective coating is highest in the case of porous materials, e.g. bituminous coatings. Seasonal cycles of dissolution of moderately and highly soluble inorganic salts during wet and colder periods and their re-crystallization, when evaporation is dominant over precipitations (Fig. 1), occur also in Slovak lowlands.

Migration of these salts in dissolved state depends mainly on drainage conditions, dynamics of groundwater

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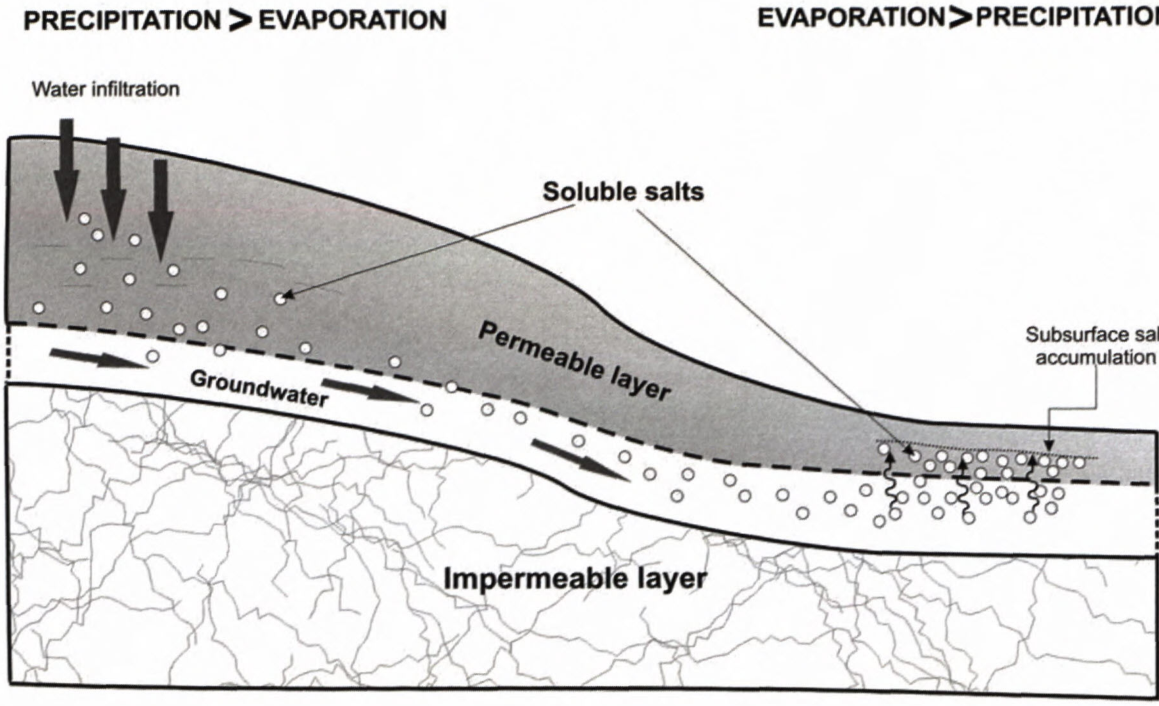

Fig. 1. Scheme of subsurface salt accumulation in soils.

flow, local geomorphology and the presence of porous permeable layers and/or seal impermeable layers. Beside climatic regime the dissolution and re-crystallization processes depend mainly on the dynamics of groundwater level changes. Corrosion affects mostly on places with failed pipeline isolation. As shown in Tab. 1, using the XRD method, the nearly mono-mineral white efflorescence of thermonatrite (Na_2CO_3 x H_2O) was identified under following conditions: Powder diffractometer DRON-3, Ni filtered CuKα radiation, measurement interval [°2Θ] of 4 to 64°. From other localities calcite, dolomite and gypsum were identified.

In natural condition the thermonatrite occurs often in association with natron Na_2CO_3 x $10H_2O$ and trona Na_2CO_3 x $2H_2O$ from which develops by partial dehydration. Under atmospheric pressure the thermonatrite precipitates from saturated solutions of soda by temperatures over 35 °C (Eugster and Smith, 1965; Last and Ginn, 2005).

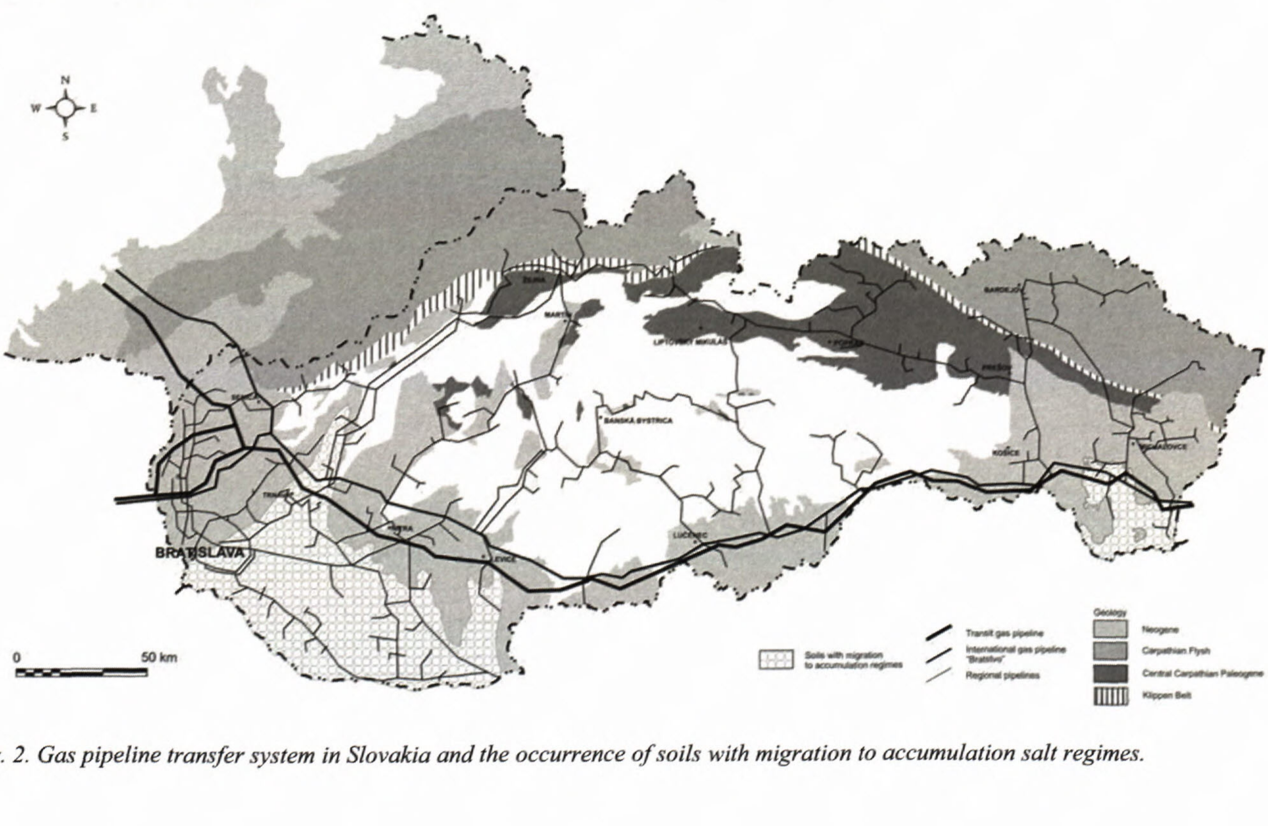

Fig. 2. Gas pipeline transfer system in Slovakia and the occurrence of soils with migration to accumulation salt regimes.

Tab. 1. Measured (m) and reference (ref) data of thermonatrite (JCPDS, 1974); d – interplanar distance, I – relative intensity.

d_{ref} [10^{-10} m]	I_{ref}	d_m [10^{-10} m]	I_m
5.352	20	5.335	33
5.240	20	5.278	30
4.720	2	4.691	12
4.120	10	4.119	23
3.240	4	3.240	12
2.768	100	2.760	100
2.753	55		
2.684	50	2.665	61
2.678	55	2.660	53
2.677	8		
2.622	8	2.638	17
2.550	2		
2.475	30	2.472	26
2.448	20	2.441	17
2.386	10		
2.372	60	2.366	57
2.238	20	2.236	18
2.181	16	2.175	14
2.065	18	2.060	18
2.026	2		
2.010	25		
2.004	20	2.004	28
1.985	4	1.984	9
1.961	4		
1.920	8	1.917	11
1.905	4		
1.875	4		

Problems of porous protective coating degradation are closely connected also by the anthropogenic, influencing the soil chemistry, i.e. mainly by the land use practice.

Occurrence of increased salt concentration in soils of Slovakia in relation to underground structures

There is up to 9 million km^2 of saline soils worldwide. The natural conditions for inorganic salt development exist in so-called saline countries with permanent or seasonal evapotranspiration regime, e.g. in Egypt and India. In EU countries the salinization influences about 1 million ha of soils mainly in Mediterranean region (Programma, 2001). In central Europe it is the case mainly in part of Hungary and Slovakia – mainly in parts of Danube and East Slovakian basins.

The accumulation of moderately and highly soluble salts and their active participation in biological and geological cycles and migration is characteristic for Slovakian lowlands. In geological conditions of alluvial regions the salt concentration is often connected with evaporative accumulation of inorganic salts. Such situations occur mostly in areas, where the groundwater level lies close to the soil surface and groundwater capillary rises to the surface. In anomalous situations the evaporative geochemical, or local redox barriers are developed. Due to the water capillary rise and evaporation the inorganic salts are accumulating near the surface residues in soil profile (Fig. 1). The extent of capillary rise is influenced mainly by the granulometry of soils and sediments (Kutílek 1978), however the whole process depends on several factors, from which the local climatic regime is the most important. More detailed criteria for mineralized water effect on secondary salt accumulation were introduced by Hraško and Bedrna (1988).

The application of agrochemicals and inconvenient irrigation water (Carter, 1969) also modify negatively the soil chemistry. Consequently, the negative effects related to underground structures became continuous. In respect to widespread and long termed agricultural activities, the increase of soil aggressiveness to steel underground constructions can reach a considerable dangerous extent. Such conditions, i.e. natural salinization combined with negative effects of salts originating from agrochemicals and irrigation are expected to occur in the most arid and hottest areas of Danube and East Slovakian lowlands (Fig. 2), especially in alluvial depressions with shallow groundwater level. The major media transfer system, i.e. oil pipe line and gas pipe line systems cross both these areas as shown in Fig. 2.

Based on the above mentioned, it is obvious that soils with accumulation of moderately and highly soluble salts (e.g. $CaCO_3$, Na-salts) in individual locations of the Danube- (Fig. 3) and East Slovakian lowlands (Fig. 4) are evaluated as potentially aggressive for porous protective coatings as shown in Fig. 5. Considering the date of steel constructions burial into the soil, the time changes of individual critical parameters are also very important.

Salt concentration changes could show long-time trends, but at the same time they would depend on seasonal changes of climatic conditions. The negative influence of mineralized soil solutions can be expected most expressive in Nové Zámky, Komárno, Kolárovo, Nitra, Trebišov, Michalovce and Kráľovský Chlmec districts. The soils in regions in Figs. 3 and 4 are of migration salt regime type according to Bedrna (1977) with alternating downward and upward movement of moderately (e.g. $CaCO_3$) and highly (sodium) soluble salts within the soil profiles. Accumulation of highly soluble sodium salts may occur especially in depressions with highly mineralized groundwater when evaporation exceeds rainfall. Occurrence of microcrystalline forms of $CaCO_3$ was described in detail by Čurlík (1992). These regions also reveal increased contents of calcium and sodium in A and C horizons of soils as shown by Geochemical atlas of the Slovak Republic (Čurlík and Šefčík, 1999).

In several localities mainly in Danube Lowland (e.g. Tvrdošovce, Nové Zámky, Komárno) the inorganic salts were identified using powder diffraction. The monomineral efflorescence of thermonatrite occurred in positions of external and internal crusts of the pipe line steel body (see Fig. 5). This section of high pressure gas pipeline was exhumed within the routine service works near

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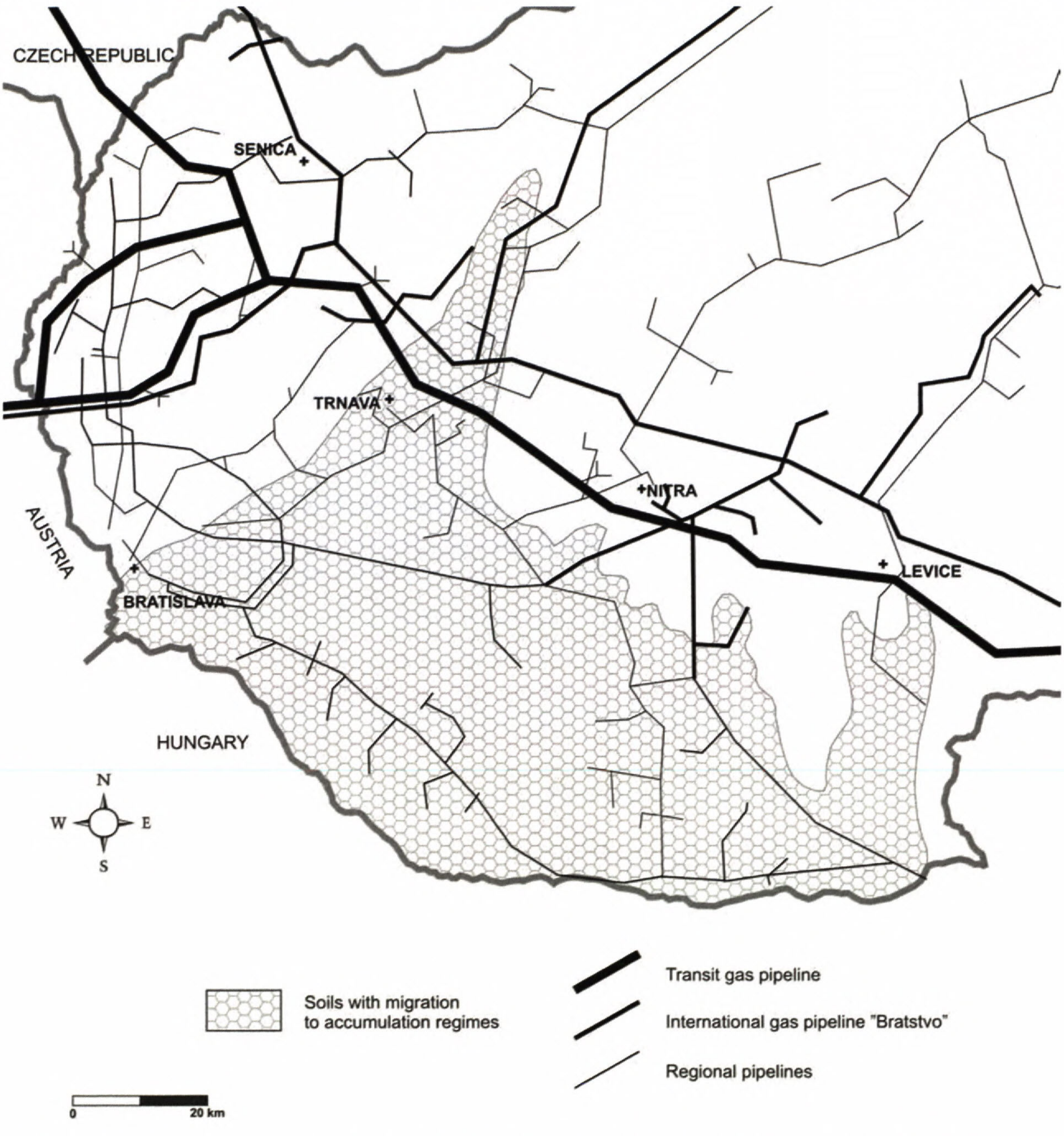

Fig. 3. Soils with migration to accumulation salt regimes in the Danube Lowland with respect to the gas pipeline system.

Tvrdošovce village in the Danube Lowland. Both, the degradation of bituminous coating and corrosion of steel body being caused also by the inorganic salts attack, are present.

Conclusions

The impact of increased salt accumulations in soil environment is in presented contribution evaluated in relation to underground structures e.g. gas- and oil pipelines. In the case of these constructions there can be distinguished a corrosion attack of inorganic salts against the metallic body as well as the degradation attack against the porous protective coatings.

Mechanism of repeated dissolution and re-crystallization of inorganic salts causes serious defects, eventually even destruction of porous protective coatings, especially in the case of bituminous isolation.

Based on the regional occurrence of soils with accumulation of moderately and highly soluble salts in Slovakia, the potential negative effect of increased salt concentrations to underground structures is expected mainly in following districts: Nové Zámky, Komárno, Dunajská Streda, Šaľa, Galanta and Senec in the Danube Basin and Michalovce and Trebišov districts in the East Slovakian Basin.

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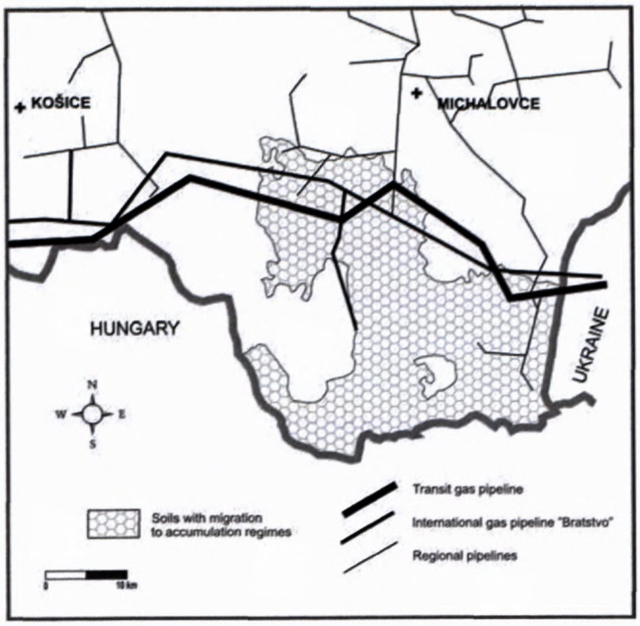

Fig. 4. Soils with migration to accumulation salt regimes in the East Slovakian Lowland with respect to the gas pipeline system.

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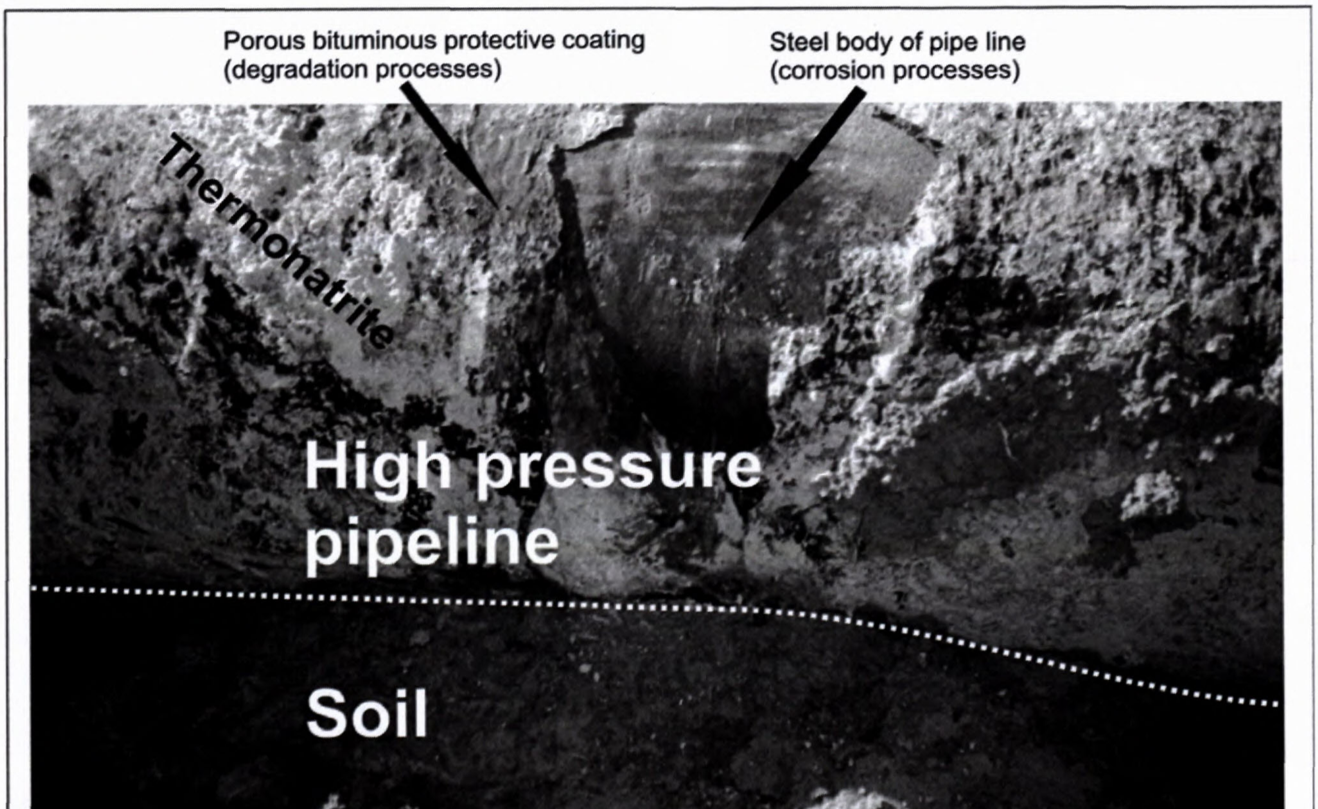

Fig. 5. Efflorescence of thermonatrite on high pressure gas pipeline in Danube Lowland.