**POVZETEK**

 Namen dela je bil raziskati mobilnost arzena v nekontrolirani deponiji piritnega pepela, ki vsebuje arzen, ter določiti njegove potencialne vplive na kvaliteto spodaj ležečih sistemov podtalnice. Raziskava je potekala tako v laboratorijskem merilu, kot tudi na deponiji.

 Preiskava terena pokaže, da deponija (50600 m3 ca.) leži na površini in obsega približno eno polovico (72300 m2) industrijske cone. 3D modeliranje lokacije pokaže, da so trije lokalni sistemi podtalnice prisotni na različnih višinah, ločeni s plastmi gline, ter da je srednji vodonosnik potencialni okoljski receptor za kontaminacijo z arzenom.

 Mineraloške in kemijske karakteristike kažejo, da piritni pepel vsebuje predvsem hematit (47%) z dodatki značilnih component tal, kot sta kremen (26%) in dolomit (21%). Elementna analiza in RTG spektroskopija pokažeta, da je celotna koncentracija arzena v materialu približno 270 mg/kg, razporejena med oksidacijski stanji As(III) in As(V) v razmerju približno 11% in 89%.

 Laboratorijski testi na sistemu piritni pepel/voda kažejo na prisotnost ravnotežja, kjer sta oba As(III) in As(V), prisotna v vodni fazi kot nevtralni H3AsO3 in anionski HAsO42-.

 Kinetični testi v vodnem mediju kažejo večjo hitrost in obseg sproščanja arzenita kot arzenata; celotna koncentracija As v ravnotežju ([As]=12 μg/L) nekoliko presega EU maksimalni dovoljeni nivo kontaminacije (MCL) za površinske vode in podtalnico, ([As]=10 μg/L). Testi z uporabo podtalnice pokažejo precej večje hitrosti sproščanja arzenata kot arzenita; celotna koncentracija As skoraj vedno presega MCL in je v ravnotežju bistveno višji ([As]=31 μg/L). Interakcije med trdno fazo in podtalnico na sami deponiji so verjetno milejše kot v laboratorijskih pogojih, zato lahko pričakujemo, da celotna koncentracija As ne dosega MCL pri izpiranju z deževnico. Pri kontaktu materiala deponije z lokalno podtalnico pa je povsem verjetno, da koncentracija As preseže MCL. Oblika kinetičnih krivulj kaže na kompleksni adsorpcijski in desorpcijski mehanizem v celotnem področju privzema in odpuščanja, verjetno z udeležbo elektrostatskih nespecifičnih vezi (outer-sphere complexes) in močnejših specifičnih vezi (inner-sphere complexes) za arzenat, ter samo specifičnih vezi za arzenit. Predpostavimo lahko tudi transportni procesi določajo procese adsorpcije in desorpcije.

 Izotermni poskusi kažejo znatno kapaciteto piritnega pepela za privzem arzena, posebno arzenita. Analiza Langmuirovih in Freundlichovih enačb, ki se ujemajo z izotermnimi podatki potrjujejo hipotezo, da je arzenat udeležen tako pri nespecifičnih kot pri specifičnih adsorpcijskih procesih na površini mineralov v piritnem pepelu, medtem ko je arzenit udeležen samo pri specifični adsorpciji. Pri implikaciji rezultatov izotermnih testov na stanje v deponiji lahko pričakujemo znatno kapaciteto piritnega pepela za vezavo obeh oblik arzena.

 Specifična geološka in hidrogeološka konfiguracija kontaminiranega mesta in ugotovljena sposobnost piritnega pepela, da vpliva na razpoložljivost arzena v vodni fazi nekoliko zmanjša potencialno nevarnost za podtalnico, kot če bi upoštevali samo količino arzena (elemental Astot=30320 kg ca.), ki je deponiran v odloženem materialu.

 To delo je prikazalo kakšen potencial ima integralni metodološki pristop s kombinacijo testiranj na terenu in laboratorijskih preiskav pri načrtovanju remediacijskih strategij.

**Ključne besede:** *piritni pepel, arzenit, arzenat, podtalnica*

**ABSTRACT**

 Objective of the research was to investigate arsenic mobility within an uncontrolled arsenic-containing pyrite ashes impoundment and the evaluation of its potential effects on the quality of the underlying groundwater systems. The research has been conducted both in-the-field and at laboratory scale.

 Elaboration of the field data shows that the impoundment (50600 m3 ca.) lies on the surface and spans ca. one half (72300 m2) of the area. The 3D modeling of the site shows that three local groundwater systems are present at different depths, separated by clay levels, and the intermediate aquifer representing a potential key environmental receptor of arsenic contamination.

 Mineralogical and chemical characterizations indicate that the pyrite ashes are mainly composed by hematite (47%) with a contribution of typical soil components, i.e. quartz (26%) and dolomite (21%). Elemental analyses and X-ray spectroscopy show that total arsenic in the material is 270 mg/kg d.m. ca., distributed between its two As(III), As(V) oxidation states in the ratio of approx. 11% and 89%, respectively.

 Lab tests on pyrite ashes/water mixtures indicate self-established equilibrium pH-Eh conditions where both As(III) and As(V) are present in the water phase, as neutral arsenite H3AsO3 and anionic arsenate HAsO42-, respectively.

 Kinetic tests in reagent water show both rate and extent of arsenite release higher than arsenate; total As concentration ([As]=12 μg/L) at equilibrium little exceeds its EU Maximum Contaminant Level (MCL) for surface and groundwater ([As]=10 μg/L). Tests in groundwater, instead, show a much higher release rate and extent for arsenate than for arsenite and the chemistry of groundwater mainly influences arsenate mobility; total As almost instantly exceeds its MCL and it is markedly higher ([As]=31 μg/L) at equilibrium. In terms of environmental implications, considering that interactions between the solid and the water phase at the site scale are probably milder than those established in the experiments, while it can be expected that the total arsenic does not top MCL in the downstream rainwater flows of the pyrite ashes deposit, a direct contact between the material and the local groundwater would, instead, make a topping of arsenic MCL in the water phase probable. The shape of kinetic plots suggests the occurrence of multiple and complex adsorption and desorption mechanisms within the entire uptake and release processes, possibly involving both electrostatically-ruled non-specific bonds (outer-sphere complexes) and more energetic specific bonds (inner-sphere complexes) for arsenate, and specific bonds only, for arsenite; the occurrence of transport-driven steps within adsorption/desorption processes can also be hypothesized.

 Isotherm experiments show a significant arsenic uptake capability by pyrite ashes, in particular for arsenite. The analysis of Langmuir and Freundlich equations fits of the isotherm data supports the hypotheses that arsenate may be involved in both non-specific and specific adsorption processes with the surface of the minerals contained in the pyrite ashes while arsenite may be involved in specific adsorption only. In terms of environmental implications of the results of the isotherm tests, should the experimental pattern approach the conditions of a possible contact between the impoundment and a water phase rich of arsenic at the site scale, a significant arsenic uptake capacity might be expected by the pyrite ashes which may act as a sink more than a source for both arsenic forms.

 The specific geological and hydrogeological configuration of the site together with the assessed capability of the pyrite ashes to influence arsenic availability in the water phases reasonably bring to predict a potential impact of the impoundment on the underlying groundwater systems less significant than that expected solely considering the amount of arsenic (elemental Astot=30320 kg ca.) contained in the disposed of material.

 Overall, the present study has illustrated the potential of the applied integrated methodological approach which, combining in-the-field investigations and lab tests at various experimental patterns, is of benefit to any plan for the environmental protection and recovery of the area and provides important information for the appropriate management of this type of industrial residue and for the definition of effective environmental protection and/or remediation strategies.

**Keywords:** *Pyrite ashes, Arsenic, Arsenite, Arsenate, Groundwater*