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انجمن بلورشناسی و کانی شناسی ایران

نقش کانی‌شناسی در مناطق متأثر از تراوش‌های طبیعی شور اسیدی، جنوب غربی استرالیا

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چکیده: مطالعهٔ تغییرات ریخت‌شناسی و کانی‌شناسی در مناطق متأثر از تراوش‌های طبیعی شور اسیدی، نشان دهندهٔ تغییرات فصلی در کانی‌شناسی سطحی است و عملکرد سولفیدی‌شدن و فرایندهای هوازدگی اکسایشی سولفیدها را منعکس می‌سازد. طی فصل مرطوب، بخش سطحی و نزدیک به سطح مناطق پوشیده از آب، عمدتاً توسط مواد سولفیدی سیاه رنگ (پیریت) و پوسته‌های نمکی، و به صورت فرعی و مقادیر بسیار کمی توسط اکسیدها و اکسی‌هیدروکسیدهای آهن مشخص می‌شود. آهن و گوگرد خارج شده از تراوش‌ها در فرایندهای سولفیدی‌شدن مشارکت می‌کنند که در کاهش شرایط احیایی در مناطق پوشیده از آب مؤثر هستند. در طول فصل خشک، کانی‌شناسی سطحی منطقهٔ تراوش طبیعی عمدتاً توسط نمکها (هالیت)، سولفاتها (ژیپس و باریت) و به ویژه ته‌نشست‌های ژله‌ای و پوسته‌های اکسی‌هیدرواکسیدهای آهن (فری هیدریت، گوتیت و شورتمانیت) مشخص می‌شود. در طول تابستان، خشک‌شدن تدریجی مناطقی که قبلاً توسط آب پوشیده شده‌اند به هوازدگی اکسایشی سولفیدها کمک می‌کند، که همراه با اکسایش سریع Fe^{2+} خارج شده از تراوش‌های جزئی که هنوز باقی مانده‌اند، باعث تشکیل اکسی‌هیدرواکسیدهای آهن و تولید اسید می‌شوند. طیف انعکاسی مرئی ـ مادون قرمز نزدیک (VNIR) از کانی‌های سطحی مناطق تحت تأثیر قرار نگرفته، پوسته شدهٔ نمکی و متأثر از تراوش طبیعی اسیدی، به دلیل جذب نوارهای اکسیدی و هیدروکسیدهای آهن، اختلاف طیفی مشخصی را در محدوده VNIR نشان می‌دهد. این اختلاف طیفی می‌تواند از طریق سنجش از دور فوق‌طیفی و چندطیفی در تهیهٔ نقشه‌های ناحیه‌ای مناطق متأثر از تراوش‌های طبیعی اسیدی و خاکهای اسید سولفاته مورد استفاده قرار گیرد.

واژه‌های کلیدی: *تراوش های طبیعی شور اسیدی، اکسی هیدروکسید آهن، طیف‌سنجی انعکاسی (VNIR)، جنوب غربی استرالیا.*

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Role of mineralogy in areas affected by natural acid saline seeps, southwestern Australia

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Abstract: The study of morphological and mineralogical changes within a natural acid saline seep affected landscape revealed that seasonal differences in surface mineralogy, reflecting the operation of sulfidization and oxidative sulfide weathering processes. During the wet season, the surface and near surface of the waterlogged seep and marsh areas is dominated by black sulfidic materials (pyrite) and minor salt crusts, with negligible iron oxides and oxyhydroxides. The Fe and S emerging from seeps contribute to the sulfidization processes operative in reducing conditions within the waterlogged zones. During the dry season, the surface mineralogy of the natural seepage zone is dominated by salts (halite), sulfates (gypsum and barite) and importantly, iron oxyhydroxides gel precipitates and crusts (ferrihydrite, goethite, schwertmannite). The gradual drying of previously waterlogged zones during summer facilitates oxidative weathering of the sulfides, which together with rapid oxidation of Fe^{2+} emerging from the still persisting minor seeps, results in the formation of iron oxyhydroxides and acid generation. The visible near infra-red (VNIR) reflectance spectra of the surface minerals from unaffected, salt crusted and acid seep areas, showed spectral differences expressed in the VNIR region due to absorption bands of iron oxides and hydroxides. The spectral difference can be utilized for regional scale mapping of acid seeps and acid sulfate soils of affected areas via hyperspectral and multispectral remote sensing.

Keywords: *Acid saline Seeps, Iron oxyhydroxide, Reflectance spectra (VNIR), Southwestern Australia.*

1. Introduction

Natural acid and saline seeps are an increasing problem in the most part of the world. They are areas of bare soil or reduced crop production, usually located on a side-hill and toe slope area. Seeps range in size from a few square meters to tens square meters, which tend to stay wet longer than surrounding areas, and may discharge water during wet seasons, while during dry seasons, white salt crystal may be visible on the surface [1]. Natural acid and saline seeps are being increasingly recognized in inland Australia, and many of such natural seeps are responsible for formation of potential acid sulfate soils [2].

The formation of saline sulfidic soils is generally related to the crystallization of iron and sulfur containing minerals [3 to 5]. The accumulation of these minerals in the soils depends very much on factors such as water flow, ionic concentration, pH and Eh [6 to 8]. These factors control oxidation states and the rate of supply of the cations and anions contributing to the growth of these minerals. The main factor responsible for formation of inland acid sulfate soils is the onset of waterlogged conditions in valleys of landforms underlain by deeply weathered regolith, which results in the mobilization of sulfur and iron from deeper regolith and accumulation of these ions in the groundwater discharge sites and in the waterlogged marshes [9].

The purpose of this study is to verify the mineralogical aspects of the precipitation in affected area by natural acid saline seeps and application of visible near infra-red (VNIR) reflectance spectra to identify seasonal changes of surface minerals.

1.1 Study area

The study area is located in the West Dale catchment, which is approximately 100 km SW of Perth, Western Australia (Fig. 1). The climate is Mediterranean and land use is dominated by pasture and grazing activities. The study area setting is typical of the region, dominated by saline groundwater seeps in the valleys, which is an increasing problem facing much of agricultural land in SW Australia [10]. In addition to saline seeps, acid sulfate soils associated with acid conditions are being increasingly recognized in inland agricultural areas of Australia [2] and are an emerging problem in the wheatbelt region of SW Australia [11].

1.2 Physiography and Geological Setting

The geology of the area is dominated by Archaean granitoids cut by NW – SE trending multiple dolerite dykes. Locally only one dolerite dyke crops out that marks a ridge, but magnetic intensity images suggest two NW-SE trending dolerites dykes and a fault [12], which is approximately 500 m to the north of the sampling locality. Geomorphologically, the area is of undulating hills with near flat hilltops and subdued but narrow valleys. Much of the area is covered by thick regolith, which can reach a depth in excess of 40 m in some valleys [13].

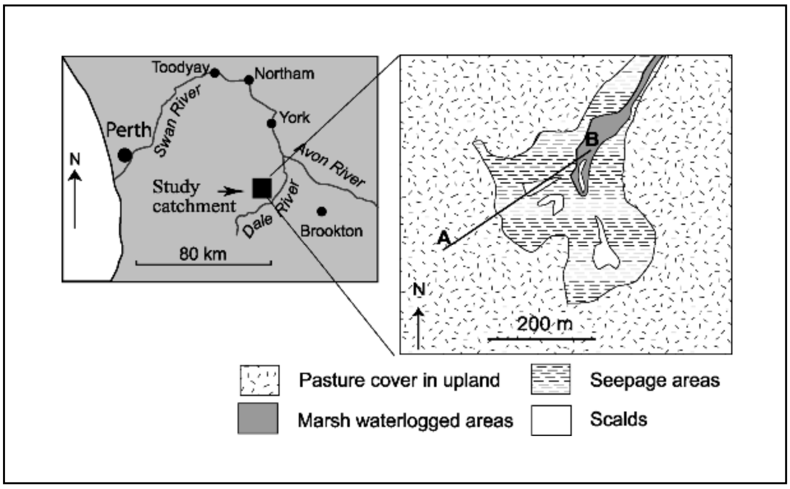

Fig. 1 Location map of the study area showing distribution of surface features. A-B is the transect for soil study shown in figure 2.

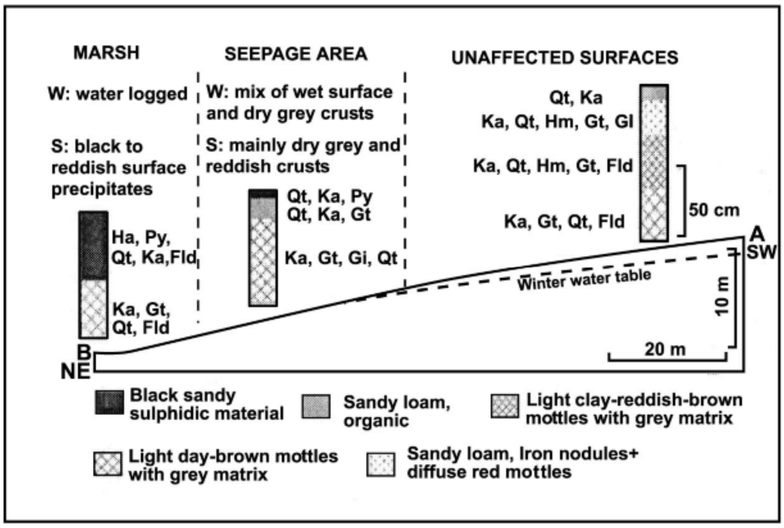

Fig. 2 A soil toposequence across the acid saline seep affected landform showing the main surface and subsurface soil morphological features. W–winter (wet) season, S–summer (dry). Mineralogy of individual soil horizon morphologies only: Qt-quartz, Ka-kaolinite, Hm–hematite, Gt–goethite, Gi–Gibbsite, Ha–halite, Py–pyrite, Fld–feldspar.

2. Study methods

Soil samples were collected by hand augering down to about 1.5 m in the marsh area. The pH and Eh of waters measured in field after calibrating the electrodes. Bulk mineralogy was determined by using X-ray diffraction (XRD) with random powder mounts as well as scanned using Cu-K_α radiation. Samples were step scanned from 4 – 80° 2θ using a 0.2° step size and with a 1 second counting time, but for some iron samples, 3 seconds counting times were employed. Diffuse reflectance spectra of surface and subsurface materials were collected with an ASD Fieldspec within the wavelength range of 350 – 2500 nm with increments of 1 nm with a 34 ms integration time. The samples for spectroscopy were dried and crushed mildly to form coarse powders. The spectra were run in a dry laboratory environment. Continuum removal procedures were not employed on the spectra. Some minerals were identified via a combination of scanning electron microscopy (SEM), both in backscatter and secondary electron mode, and energy dispersive X-ray analysis (EDX). Some sulfidic samples were studied in a moist, uncoated state in the SEM, which reduced resolution of the images.

3. Results

3.1 Toposequence characteristics of regolith

Based on the nature of the surface and groundwater conditions, the landsurface divided into three areas along the toposequence: unaffected zone in the upper catchment, seepage zones in the mid slope, and permanently waterlogged zone (marsh) in the valley floor (Fig. 2); This classification is similar to landform settings of many inland acid seeps and potential acid sulfate soils in Australia [9]. The affected land area is represented by the waterlogged and seepage zones migrate upwards into the toposequence; therefore gradually increasing the degraded land area and reducing pastures. Six soil profiles were sampled and studied along a toposequence, but the locations and morphological properties of only three profiles, representative of the three main landscape positions, are shown in Figure 2.

3.2 Dry unaffected zones (upper catchment)

Grassland or pastures dominate the surface of topographically higher unaffected land. The soils in the unaffected part are duplex and sandy loams, with red to dark red nodules in the B horizon grading into reddish mottles and eventually into brown to dark brown mottles with grey matrix colours in the C horizons (> 80 cm). The dominance of gley colours coincides with winter perched groundwater levels. Some sub-vertical mottles along voids are present. The nodules and various mottles (pore linings and Fe masses) are redoximorphic features indicative of oxidation-reduction conditions in a saturated environment [14]. The mineralogy of individual horizons is shown in Figure 2, with the secondary iron minerals showing a gradual change from dominant hematite in the reddish nodules near the top to dominant goethite lower down in the brown mottles.

3.3 Seepage zones (mid slope)

During winter, the seep zones are saturated and have either micro-relief soggy areas with blackish material mixed with bare grey crust scalds. In summer, the same seepage areas are considerably drier, have reddish-brown and grey crusts with only minor seeps emerging at the surface. Many parts of seepage zone have hard, bare localized patches or scalds interspersed with rills and gullies. The rills are a few centimetres in depth and occur along the slopes where seeps emerge, and gullies around 2 m wide and up to 1 m deep dominate the valley floor. During winter, the pH of seeps is > 4.5 while in summer it drops to < 3.5. The morphology and mineralogy of soil profiles underlying the seepage zone are similar to the unaffected zone, except that a dark A horizon is present in the seepage zone (Fig. 2). The main difference is the presence of minor quantities of pyrite in the dark surface material. The differences in morphology of surface material during winter and summer are expressed in the differences in mineralogy, with reddish crusts being dominated by ferrihydrite (6-line), halite, gypsum and minor schwertmannite and goethite (Table 1).

3.4 Marsh zones (valley floors)

During winter, the marsh area is waterlogged and mostly submerged. During summer, parts of the marsh zone dry up and have reddish to black surface crusts, while parts remain waterlogged. The pH of water in the marsh areas is > 5.5 in both winter and summer, but with reducing conditions (Eh~ -20 mV). The marsh area profiles have 30-60 cm thick black “ooze” type material which when disturbed emanates a strong rotten egg smell, indicative of black sulfidic material as observed by Fitzpatrick [9]. Below this sulfidic material, brown to dark brown mottles in a grey matrix dominate. The nodules and mottles are redoximorphic features that relate to saturation and redox conditions. Moist, uncoated sulfidic materials observed with the SEM revealed sub-rounded particles composed of sulfur and iron and interpreted as pyrite (Fig. 3), and presence of pyrite was confirmed by XRD. These particles could be an agglomeration of smaller particles. In winter, much of the seep and marsh area is saturated and only blackish material and minor halite are present on the surface.

Table 1 Mineralogy as determined by XRD, of the different surface precipitates within the seep and marsh area during dry summer month.

Surface morphology	**Mineralogy**
Dry grey crusts	Halite, gypsum, barite, kaolinite, quartz
Reddish crusts	Ferrihydrite, schwertmannite, halite, gypsum, quartz
Reddish gelatinous precipitates	Ferrihydrite, schwertmannite, goethite, halite, gypsum

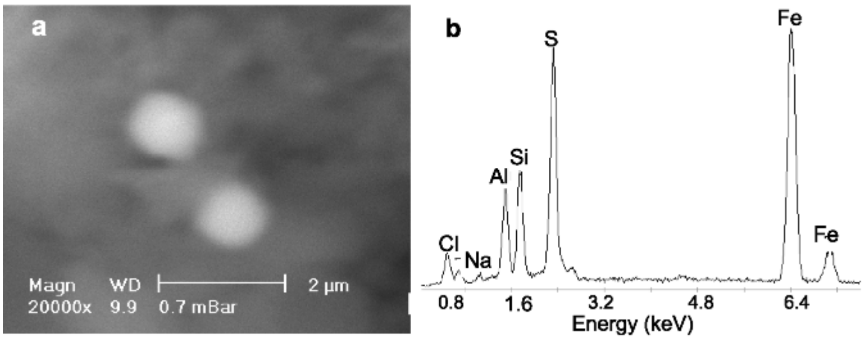

Fig. 3 (a) SEM backscatter image of black sulfidic material from the marsh area showing sub-rounded bright, high atomic number particles. (b) EDX spectrum of the brighter particles indicating S and Fe (pyrite). The other minor spectrum peaks are from kaolinite (Al and Si) and halite (Na and Cl) from the surrounding material

3.5 Reflectance spectroscopy (VNIR)

The reflectance spectra of surface materials collected in summer from the unaffected land, the seepage area (grey and reddish crusts), and the marsh area (black sulfidic materials), showed marked differences according to their mineralogy. Figure 4 shows the diffuse reflectance spectra of the three different surface materials: the reddish crust (seepage zone), grey scalds (seepage zone) and black surface (seepage and marsh zone). The grey scald area shows absorption features representative of presence of minor amounts of kaolinite (Al-OH vibrational modes at 2200 nm) and none indicative of halite, because of the lack of absorption features from chloride minerals within the observed wavelength range. The reddish crusts present in some minor active seeps and ubiquitous in the dried seep areas show broad absorption features around 900 nm. These wavelength features are assigned to the crystal field transitions of ferric iron (6A1g → 4T2g transition), and a subtle shoulder at 640 nm due to the 6A1g → 4A1g transition [15]. The broad and intense absorption peaks at 1400 & 1900 nm are indicative of molecular vibration transitions of bound water. The iron crust spectra correspond to those of ferrihydrite reference spectra [16], and possibly a shoulder at 640 nm indicative of schwertmannite. The high amount of bound water suggests that the material is dominated by ferrihydrite with lesser amounts of schwertmannite, and XRD of the same material confirmed this interpretation (Table 1).

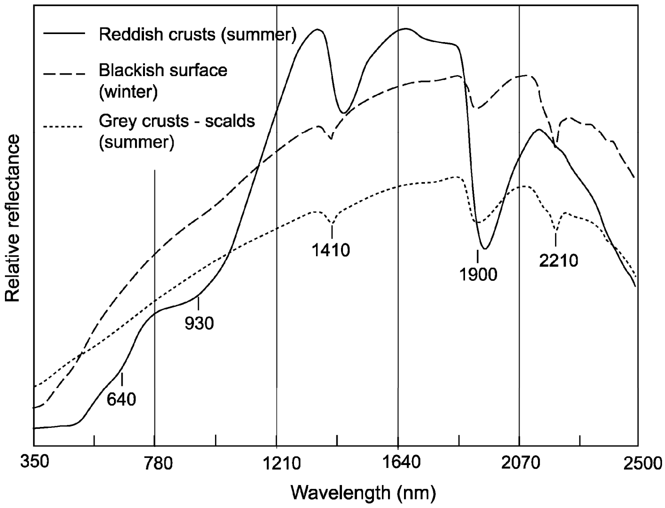

Fig. 4 Reflectance spectra in the UV-visible-near infrared range of different surface materials in summer and winter months. The positions of visible wavelength region reflectance minima (before continuum removal) are indicated.

4. Discussion

The differences in morphology and mineralogy of the surface and near surface materials during the wet winter and dry summer indicate the operation of seasonal dynamic groundwater and geochemical processes, that are expressed in the surface and near surface soil mineralogy. During the wet winter months, water tables are higher with redoximorphic features (mottles, nodules, pore linings) forming in response to saturation and reducing-oxidation conditions within the subsolum. The presence of hematite and goethite in the subsolum of the entire toposequence indicates operation of redox conditions in the area with high water table.

The presences of pyrite bearing black sulfidic materials in the waterlogged marsh areas (valley floors) indicate the formation of pyrite within the upper horizons of the submerged soils, dominantly during winter. Iron and Sulfur, released from the topographically higher regolith profiles in response to rising water tables due to deforestation, are responsible for the formation of sub-micrometer pyrites grains, which a reaction that is catalyzed by microbial processes and organic matter at or near the surface. The oxidation of Fe^{2+} emerging from the seeps is restricted due to waterlogged and reducing conditions prevailing on and near surface. The significant changes in surface material during summer in the seepage zone indicate the operation of two processes that linked to the drying of the surface (lowering of perched water table) and onset of oxidizing conditions, both being responsible for increasing acidity.

Firstly, in contrast to wet water logged surfaces, the emergence of Fe^{2+} in the seeps results in rapid oxidation and hydrolysis of iron leading to formation of ferrihydrite and goethite as precipitates, and subsequent increase in H^+, a reaction similar to the first part of ferrolysis. Secondly, drying of much of the seep area and marsh area leads to oxidation of near surface sulfidic material, followed by Fe^{3+} hydrolysis and resulting in the formation of ferruginous precipitates and creation of acid conditions in the regolith, stream and shallow groundwater [9]. Complete drying results in the formation of crusts with ferrihydrite, goethite, halite, gypsum and barite that precipitate in relation to evaporation.

The understanding of the seasonal processes and its effect on surface and near surface mineralogy are critical to the recognition and management of an increasing number of acid saline seeps across the vast land area of the West Australian wheatbelt, as opposed to the much publicized salinity issues. Firstly, the recognition of surface ferruginous minerals via spectral reflectance in summer months will enable the use of hyperspectral and multispectral remote sensing to cost effectively identify and monitor acid generation areas and acid sulfate soils (discriminated via presence of surface iron oxyhydroxides in summer months), as opposed to purely saline seeps that are dominated by halite.

Such mapping of acid areas via surface mineralogy has been applied to acid mine drainage environments [17].

Secondly, the hematite-goethite ratio with respective hues and chromas [14] in soil profiles can be used as indicators of saturation state during any month, and used to estimate waterlogging conditions in particular parts of the landform. Thirdly, the iron oxide and hydroxide minerals found in soils and surface precipitates act as metal adsorbants [18], and their solubility during different seasons will affect metal concentrations of surface and groundwater. However, to fruitfully apply the rapid but robust methods of spectral reflectance of minerals to land management issues, it is imperative to understand the processes by which the minerals form, and then accordingly formulate and implement land and water management strategies.

5. Conclusions

This study demonstrates dynamic, seasonally influenced changes to surface and near surface mineralogy of an acid saline seep affected landform. During the wet months, due to waterlogging, the sulfidization process dominates, while during the drier months, oxidative weathering of pyrite and iron hydrolysis results in precipitation of iron oxyhydroxides at and near the surface with the generation of acidity. The study found the iron oxyhydroxide minerals present in the surface crusts and precipitates reflect acid conditions, as opposed to halite and gypsum that reflect only saline conditions. This difference in the surface mineralogy during summer months can be readily identified via multispectral and hyperspectral remote sensing methods mainly during summer, and therefore regionally mapped to identify spatial and temporal distribution of acid seeps.

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References

[1] Schrock M., Mankin K., Lamond R., *"Controlling saline seeps"*, Kansas Stata University, Agricultural Experiment Station and Cooperative Extension Service, MF-2391, Soil Management (1999) 4 pp.

[2] Fitzpatrick R. W., "*Inland acid sulfate soils: A big growth area*", In 5th International Acid Sulfate Soils Conference, Tweed Heads, NSW (Book of Extended Abstracts) (2002).

[3] Berner R. A., *"Sedimentary pyrite formation, Am"*, J. Sci. 268 (1970)1-23.

[4] Fanning D. S., Fanning M. C. B., *"Soil morphology, genesis, and classification"*, Wiley, New York. (1989).

[5] Schwertmann U., Fitzpatrick R. W., "*Iron minerals in surface environments"*, ed. by: Skinner H. C. W., Fitzpatrick R. W., *"Biomineraliz-ation processes of Iron and Manganese – Modern and ancient environments"*, Catena Suppl. 21 (1992) 7-30.

[6] Van Breemen N., *"Effects of seasonal redox processes involving iron on the chemistry of periodically reduced soils"*, ed. by: Stucki J. W., Goodman B. A., Schwertmann U., *"Iron in soils and clay minerals"*, Reidel, Dordrecht (1988) 797-842.

[7] Brinkman R., Pons L. J., *"Recognition and predication of acid sulfatesoil condition"*, ed. by: Dost H., *"Acid sulfate soils"*, ILRI Publ. 18, Wageningen (1973) 169-203.

[8] Naidu R., Fitzpatrick R. W., Hudnell W. H., *"Chemistry of saline sulphidic soils with altered water regime in the Mount Lofty Ranges, South Australia"*, ed. by: Monchareon L., et al., Proc. Int. Symp. *"On Strategies for Utilizing Salt Affected Lands"*, Bangkok, Thailand (1992) 477-480.

[9] Fitzpatrick R. W., Fritsch E., Self P. G., *"Interpretation of soil features produced by ancient and modern processes in degraded landscapes: V Development of saline sulfidic features in non-tidal seepage areas"*, Geoderma 69 (1996) 1-29.

[10] George R. J., McFarlane D. J., Nulsen R. A., *"Salinity threathens the viability of agriculture and ecosystems in Western Australia"*, Hydrogeology Journal 5(1997) 6-21.

[11] George R. J., *"Secondary acidification an emerging problem in wheatbelt"*, Focus on Salt 23(2002) 10.

[12] Edkins R., *"Westdale focus group catchment report, Salinity Action Plan"*, Australian gov. Report (1998).

[13] Lewis M. F., McConnel C. E., *"Observations on groundwater recharge in the Westdale catchment. Agriculture, Western Australia"*, Resource Management Technical Report 180 (1998).

[14] Bigham J. M., Fitzpatrick R. W., Schulze D.,*"Iron Oxides"*, ed. by: Dixon J. B., Schulze D. G., *"Soil Mineralogy with Environmental Applications"*, Soil Science Society of America Special Publications. Madison, Wisconsin, USA (2001) 323-366.

[15] Cudahy T., Ramanidou E., *"Measurement of the hematite :goethite ratio using field visible and near-infrared reflectance spectrometry in channel iron deposits*, *WA. Australian"*, Journal of Earth Sciences (1997) 411-420.

[16] Crowley J. K., Williams D. E., Hammarstrom, J. M., I-Ming C., Mars J. C., *"Spectral reflectance properties (0.4-2.5 μm) of secondary Fe-oxide, Fe-hydroxide, and Fe-sulphate –hydrate minerals associated with sulphide-bearing mine wastes"*, Geochemistry: Exploration, Environments and Analysis 3 (2003) 219-228.

[17] Swayze G. A., Smith K. M., Clark R. N., Sutley S. J., Pearson R. M., Vance J. S., Hageman P. L., Briggs P. H., Meier A. L., Singleton M. J., Roth S., *"Using imaging spectroscopy to map acidic mine waste"*, Environmental Science and Technology 34 (2000) 47-54.

[18] Manceau A., Marcus M. A., Tamura, N., *"Quantitative speciation of heavy metals in soils and sediments by Synchrotron X-ray Techniques"*, ed. by: Fenter P. A, Rivers M. L., Sturchio N. C., Sutton S. R, *"Applications of synchrotron radiation in low-temperature"*, geochemistry and environmental science (eds) (2002) 341-428.