

کانی‌شناسی سطحی خاک‌های سولفات‌ه اسیدی ساحلی، در ناحیه شهری پینجارا، جنوب غربی استرالیا

مصطفی رقیمی*

گروه زمین‌شناسی، دانشگاه گلستان - گرگان

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چکیده: خاک‌های سولفات‌ه اسیدی در استرالیا عموماً در مناطق ساحلی قرار دارند. یکی از بزرگترین تهدیدات در محیط ساحلی بهم خوردگی خاک‌های سولفات‌ه اسیدی در اثر توسعه شهری است، که منجر به اسیدی شدن گسترده زمین‌ها، نهرها و در نتیجه خسارت‌های اقتصادی در همان مکان یا در مناطق همجوار می‌شود. نمونه‌برداری سطحی از اشکال زمین مختلف در منطقه مورد مطالعه و نتایج آزمایش‌های XRD، SEM و VNIR بیانگر تغییرات ریخت‌شناسی و کانی‌های سطحی در مناطق تحت تأثیر ناشی از فرآیند هوازدگی اکسایشی سولفیدی است. در طی فصل خشک، کانی‌شناسی منطقه متأثر از نمک با هالیت، ژیپس، باریت و به‌ویژه پوسته‌های اکسی هیدروکسیدهای آهن (فری هیدریت و شورتمانیت) مشخص می‌شود. هوازدگی اکسایشی جاروسیت با اکسایش سریع Fe^{2+} می‌تواند سبب تشکیل اکسی و هیدروکسیدها آهن و اسید گردد. طیف انعکاسی مرئی - مادون قرمز نزدیک (VNIR) از منطقه متأثر از نمک و افق خاک‌های سولفات‌ه اسیدی، به دلیل جذب نوارهای اکسیدی و هیدروکسیدهای آهن، اختلاف طیفی مشخصی را در محدوده VNIR نشان می‌دهد. این اختلاف طیفی می‌تواند برای نقشه‌برداری از بهم خوردگی خاک‌های سولفات‌ه اسیدی ساحلی در اثر شهرسازی در مقیاس ناحیه‌ای از طریق روش‌های دورسنجی چند طیفی و فوق طیفی در ناحیه پینجارا استفاده گردد.

واژه‌های کلیدی: خاک‌های سولفات‌ه اسیدی ساحلی، کانی‌شناسی سطحی، شهری، جنوب غربی استرالیا.

* نویسنده مسئول، تلفن: ۴۴۲۷۰۵۰ (۰۱۷۱) ۹۸+، نمابر: ۴۴۲۷۰۵۰ (۰۱۷۱) ۹۸+، پست الکترونیکی: raghimi@yahoo.com

Surfacial mineralogy of coastal acid sulfate soils in urbanization area of Pinjarra, Western Australia

Mostafa Raghimi*

Department of Geology, University of Golestan, Gorgan, Iran.

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Abstract: Acid sulfate soils in Western Australia commonly occur in coastal regions. One of the greatest threats to coastal environment is the disturbance of acid sulfate soils due to urban development which can lead to widespread acidification of lands and streams and subsequent economic losses onsite or in adjacent areas. Surface sampling from different landforms of the study area and analytical results of XRD, SEM and VNIR indicate that morphological and surfacial minerals variations, due to oxidative sulfide weathering processes in affected landscape. In dry season, the surface mineralogy of salt affected zone is dominated by halite, gypsum, barite and importantly, iron oxyhydroxides crusts (ferrihydrite, schwertmannite). The oxidative weathering of the jarosite with rapid oxidation of Fe^{2+} , can generate iron oxyhydroxides and acid. The visible near infra-red (VNIR) reflectance spectra of the surface minerals from salt affected zone and acid sulfate soils horizon, 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 coastal acid sulfate soils disturbance due to urbanization in Pinjarra area via hyperspectral and multispectral remote sensing.

Keywords: *Coastal acid sulfate soils. Surface mineralogy, Urbanization, Southwestern*

Introduction

Australian acid sulfate soils weathering environments could be placed into three grouped including coastal acid sulfate soils (tidal mangrove swamps) [1, 2], inland acid sulfate soils (non-tidal scalds driven by saline acid-sulfate discharge conditions)[3,4] and minesite acid sulfate soils (waste rock stockpiles or tailing impoundments) [5, 6]. Coastal acid sulfate soils have formed through natural processes and are generally overlain by other soils. However, when coastal acid sulfate soil are exposed by drainage or excavation and then rewetted, acid drainage water is produced. Past government policies, the high demand for living on the coast and the extensive agriculture along the coastal strip, have led to disturbance and increased exposure of acid sulfate soil. These have resulted in large-scale acid generation and runoff [7]. The unique properties of coastal acid sulfate soil arise from their sulfide content. Sulfide concentrations (as pyrite) range

from about 0.01 per cent to as high as 15 per cent. Not all acid produced by oxidation of sulfides is released into streams because the acid soil water can react chemically partly or even completely with the sediments in which it was produced. The reaction between acid and soil constituents, mainly clay minerals, liberates dissolved aluminum, iron, manganese, heavy metals such as arsenic and copper into soil and drainage waters. These ions remain dissolved, provided the solution remains acid (pH generally less than 4.5), and can be extremely toxic to plants and killed organisms [8].

In Australia iron sulfide layers are found along the coastlines of the Northern Territory, Queensland and New South Wales. They are also found along the northern coastline of Western Australia (around Perth), Adelaide and Westernport Bay near Melbourne [9]. The current principal land uses in coastal ASS areas include [7]: Agriculture, Urban development, Infrastructure, Aquaculture, Mining and

Undeveloped areas. However, developments on ASS, particularly large scale drainage and flood mitigation schemes, can lead to widespread acidification of land and streams and subsequent economic losses onsite or in adjacent areas [10]. This paper deals with the formation of surfacial mineralogy on disturbed coastal acid sulfate soils land use due to urbanization in Pinjarra area in Western Australia.

Study area

The study area is located in South of Perth city, Western Australia which is located on Pinjarra Plain in eastern part of Peel-Harvey estuary (Fig 1). This estuary has been described at the regional scale [11]. The main regional geomorphic components framing the system area: a barrier ridge of spear wood dunes; Aeolian and fluvial low lands of Bassendean dunes and Pinjarra plain; and riverine discharge points. These units have an influence on the development of coastal landforms and sediments along the estuary shore. [12].

Climate and Hydrology

The climate of the area is subtropical, with hot dry summers and wet mild winters [13]. Rainfall is moderate, *app.* 825 mm/yr, falling mainly in May to October [14].

The estuarine system is receiving basin for meteoric, fluvial, marine and ground waters, and peripheral wetlands of the area are maintained by one or more of these hydrological sources. Rainfall accounts for 20% to 30% of the fresh water input,

while rivers and groundwater discharge account for the rest [15]

Study methods

Ten different surface samples from salt affected area and acid sulfate soils horizon in the study area have been collected. Bulk mineralogy of five samples, after preparation were determined, by using X-ray diffraction (XRD) of Phillips 400 at CSIRO of Western Australia with random powder mounts as well as scanned using $\text{CuK}\alpha$ radiation. Samples were step scanned from $4 - 80^\circ 2\theta$ 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 materials one from salt affected area and another one from acid sulfate soils horizon 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 for study the visible near infra-red (VNIR) reflectance spectra. 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 from one of the salt affected collected samples were identified via scanning electron microscopy (SEM) of Goel 3000 in CSIRO of Western Australia. Samples were studied in a dry, coated state with gold coating in the SEM.

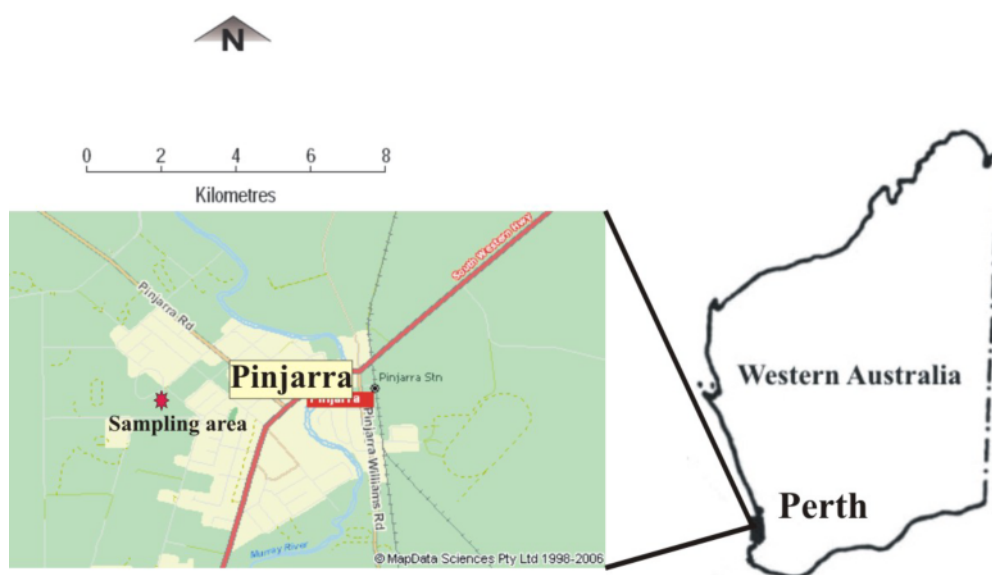


Fig. 1 The location map of Pinjarra city and sampling area

Results

Based on the nature of the surface of the study area, the land surface divided into two areas salt affected area and acid sulfate soil horizon. The salt affected land area is represented by gradually increasing the degraded land area and reducing pastures, while acid sulfate soil horizon mostly in small brooks ditched area (Fig 2).

Salt affected area

During dry season, with bare grey to white crust scalds. These whitish grey crusts contain hard, bare localized patches or scalds interspersed with rills. The rills are a few centimetres in depth and occur

along the slopes where seeps emerge on the surface.

The morphology and mineralogy of salt affected zone, show the presence of whitish crusts which being shown by halite, gypsum and barite (Fig. 3).

Acid sulfate soils horizon

The nodules and mottles features of jarosite minerals can be related to oxidation condition, which could be seen in trenched and digging profiles (fig. 4). Presence of jarosite was confirmed by XRD (fig.5). These particles could be an agglomeration of smaller particles which embedded in marine sediments.



Fig. 2- **a.** Degraded land due to salt affected area in Pinjarra area, **b.** Acid sulfate soil horizon in ditched area in Pinjarra area

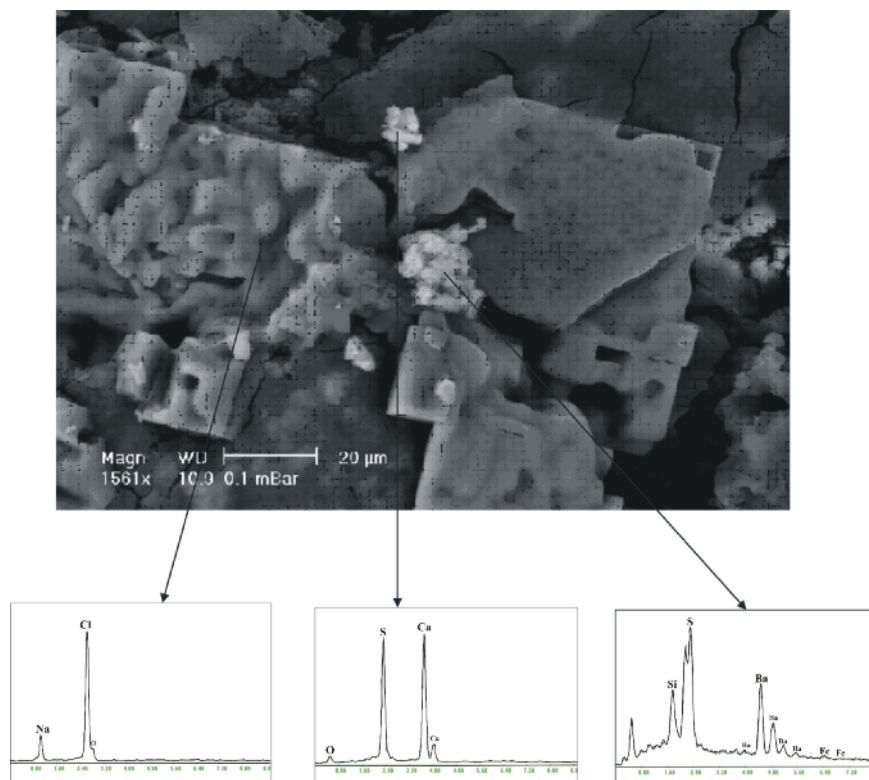


Fig. 3 A) SEM backscatter image of salt affected area. B) EDX spectrum of the brighter particles indicating barite (S and Ba), gypsum (S and Ca) and halite (Na and Cl)



Fig. 4 The presence of jarosite mineral (yellowish color) in acid sulfate soils horizon

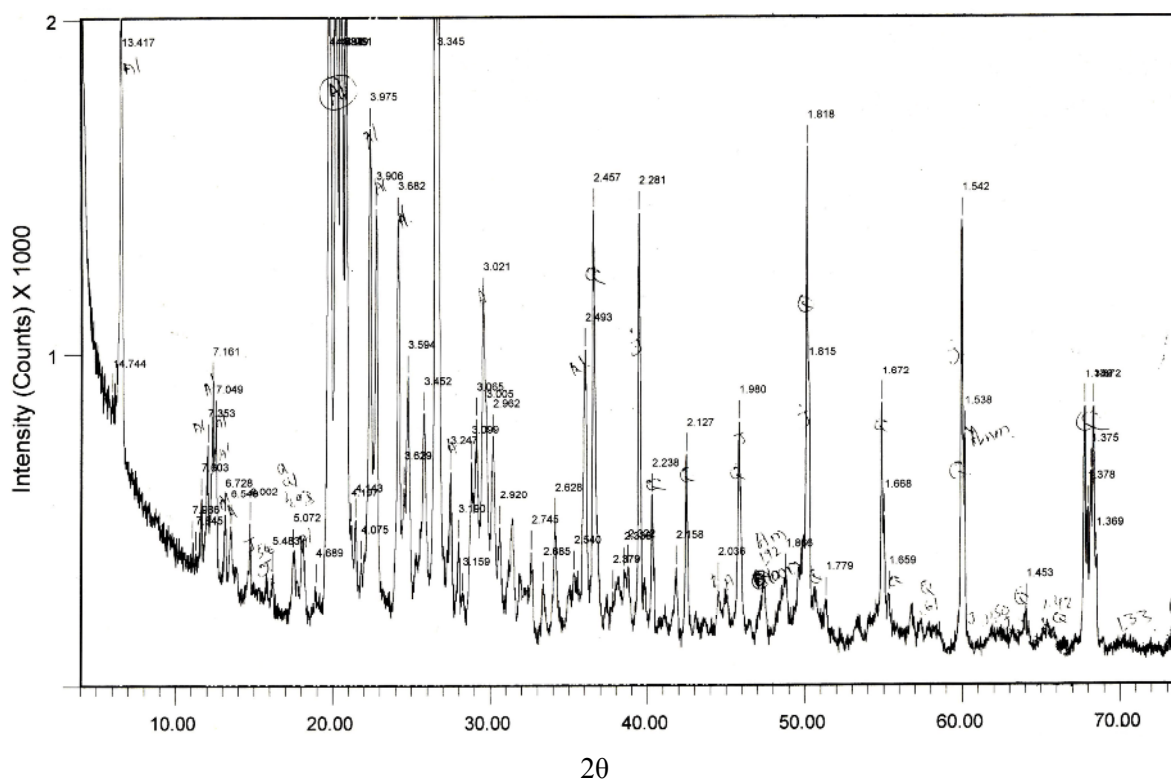


Fig. 5 XRD diagram of acid sulfate soils sample showing presence of jarosite mineral (the yellowish material from spot in fig. 4)

Reflectance Spectroscopy (VNIR)

The reflectance spectra of two surfacial samples, which have been collected from salt affected land and acid sulfate soils horizon, showed marked differences according to their mineralogy. Figure 6 shows the diffuse reflectance spectra of the two different surface materials: the reddish crust (Acid sulfate soils horizon zone) and whitish grey scalds

(salt affected area). The whitish 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 Acid sulfate soils horizon show broad absorption features around 900 nm.

These wavelength features are assigned to the crystal field transitions of ferric iron (${}^6A_{1g} \rightarrow {}^4T_{2g}$ transition), and a subtle shoulder at 640 nm due to the ${}^6A_{1g} \rightarrow {}^4A_{1g}$ transition [16]. 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 [17], and possibly a shoulder at 640 and 1455 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 (Fig 7).

Discussion

Due to the mode of geological data, the majority of potential acid sulfate soils are found along the coastal plains of Western Australia. The formation of such acid sulfate soils have been formed by sulfidization processes at postsulfurization stage. The formation of jarosite mineral could be occurred as weathering of pyrite by the hydrolysis of iron at low pH [18]. The productions of new mineral phases are formed as a result of dissolution

[19]. In the acid sulfate soils horizon of studied area, presence of jarosite aggregate minerals which formed in marine sediments could be seen (Fig 4). Such jarosite mineral presumably formed during the active stage but remains in the soils for long periods after the active sulfurization has ceased. Commonly, soil materials representing the active and presulfurization stages underlie materials that represent the postsulfurization stage [20]. According to Fanning and Fanning [21] who described acidic waters resulting from the oxidation of iron sulfides may precipitate a large number of secondary iron phases such as melanterite, rozenite, ferroxahydrate, copiapite, jarosite, and amorphous iron. All of these solid phases are very soluble except jarosite and amorphous iron. Several studies have been completed on the solubility relationships and precipitation of jarosite in acidic waters [22]. As iron is oxidized and hydrolyzed, various iron minerals form in the soil including ferrihydrite and schwertmannite, If the soil pH falls below four while maintaining an oxidizing environment then the mineral jarosite can be formed (Fig 8) [23].

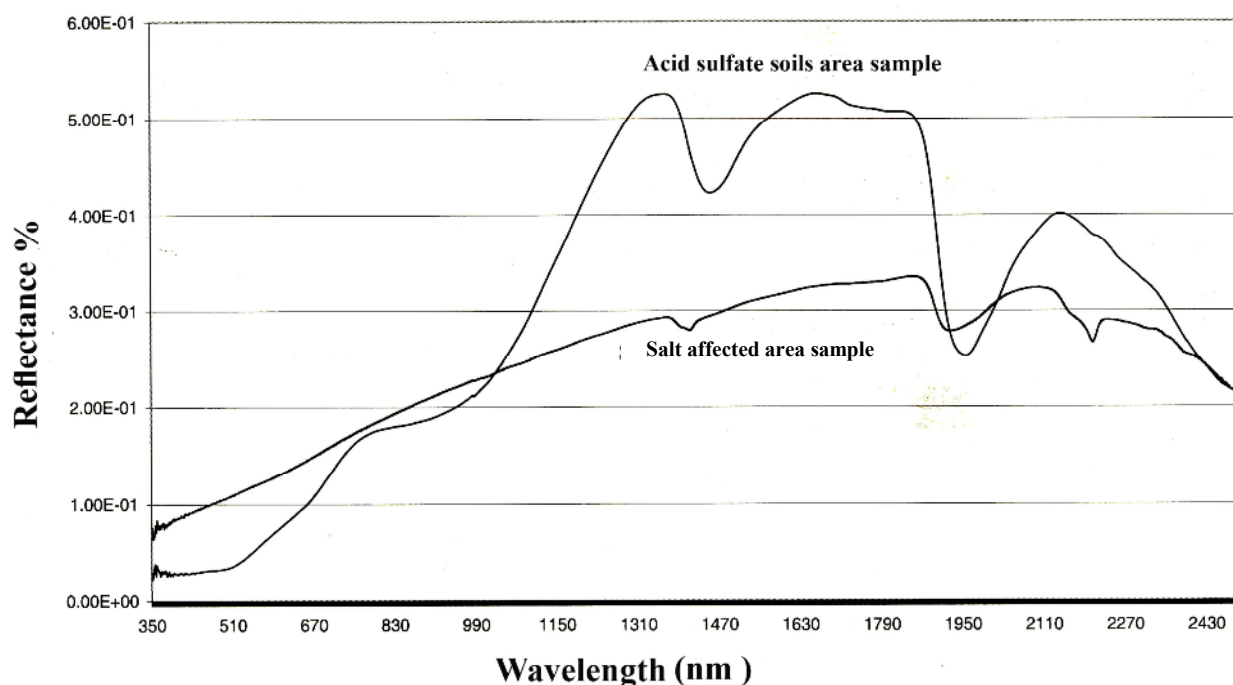


Fig. 6 Reflectance spectra in the UV-visible-near infrared range of surface materials in salt affected area and acid sulfate soils horizon

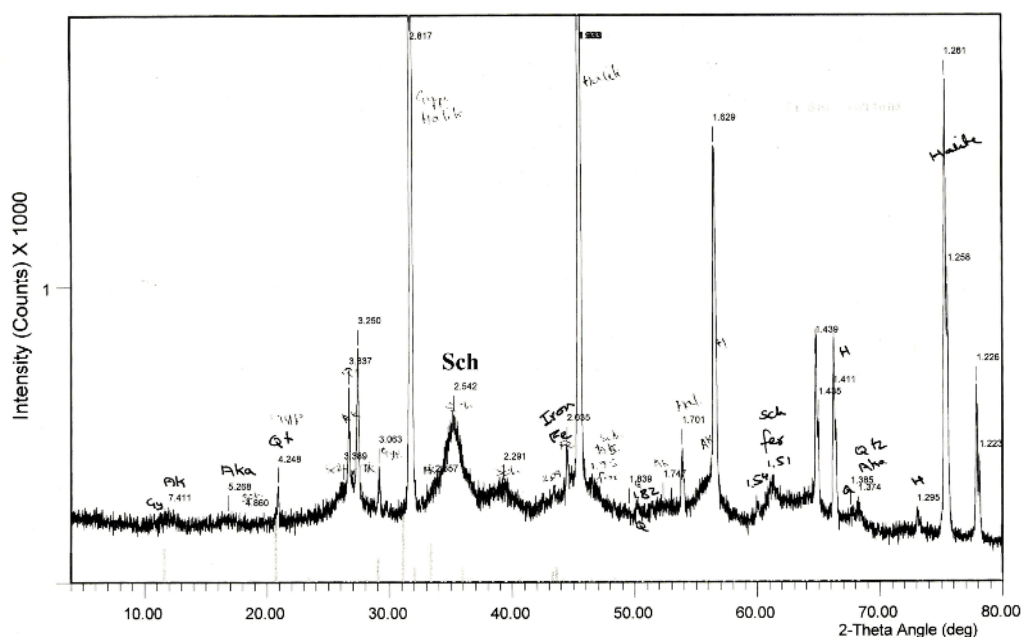


Fig. 7 XRD diagram of acid sulfate soils sample showing presence of schwertmannite (Sch) mineral

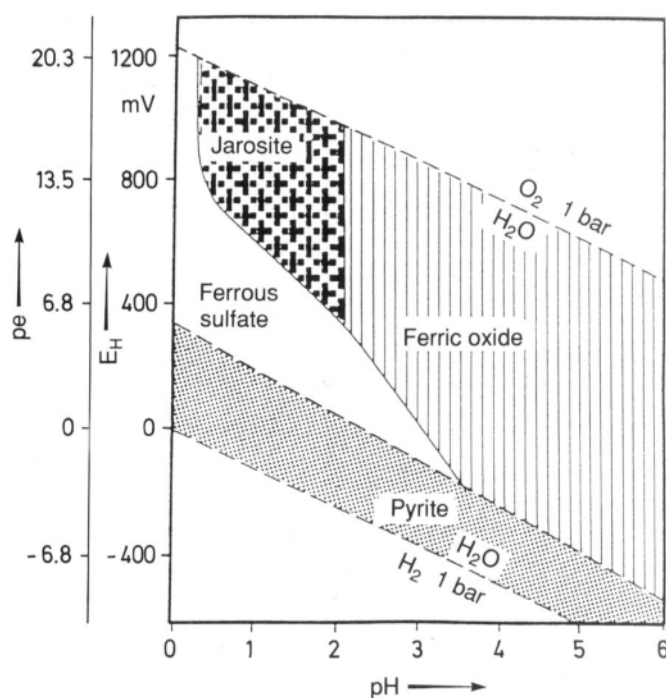


Fig.8 Eh-pH diagram showing stability fields for oxidation-reduction-sensitive constituents found in acid sulfate soils under certain assumed boundary conditions [21]

Because jarosite forms under conditions of high Eh and very low pH, which can only develop from the generation of sulfuric acid, it is considered a diagnostic mineral for acid sulfate soils [Fanning, 2001]. Subsequently, the soil pH has risen due to

weathering of silicate minerals or addition of eolian carbonates. Because the redox potential has remained strongly oxidized, the jarosite has persisted as a metastable piece [24]. In this study, during postsulfurization, sulfuric acid has been

generated in large amounts in the past, but the present rate of acid generation is negligible. The resulting pH is typically 4 or above.

The differences in morphology and mineralogy of the surface indicate the operation of seasonal dynamic groundwater and hydrogeochemical composition 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 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 ferrolisis. Secondly, drying of much of the seep and marsh areas lead 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 [25]. 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 [26]. Secondly, the hematite-goethite ratio with respective hues and chromas [27] 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 [28], 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.

Conclusions

This study demonstrates dynamic influence of changes to surface and near surface mineralogy of a landform. The study found the iron oxyhydroxide minerals present at the surface crusts and precipitates reflect acid conditions, as opposed to halite and gypsum that reflect only saline conditions. The surface mineralogy during summer can be readily identified via multispectral and hyperspectral remote sensing methods, and therefore regionally mapped to identify spatial and temporal distribution of acid seeps. The location of acid sulfate soils and an understanding of the processes involved during their disturbance in coastal area change the land use due to urbanization the area under study needs to manage the deleterious impacts of acid sulfate soil disturbance on water quality. These impacts reduce the ecological, commercial and recreational value of coastal waterways in Western Australia.

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