Characterization of Saudi Red Mud to prepare ceramic coating to protect external surface of water and waste water pipe lines

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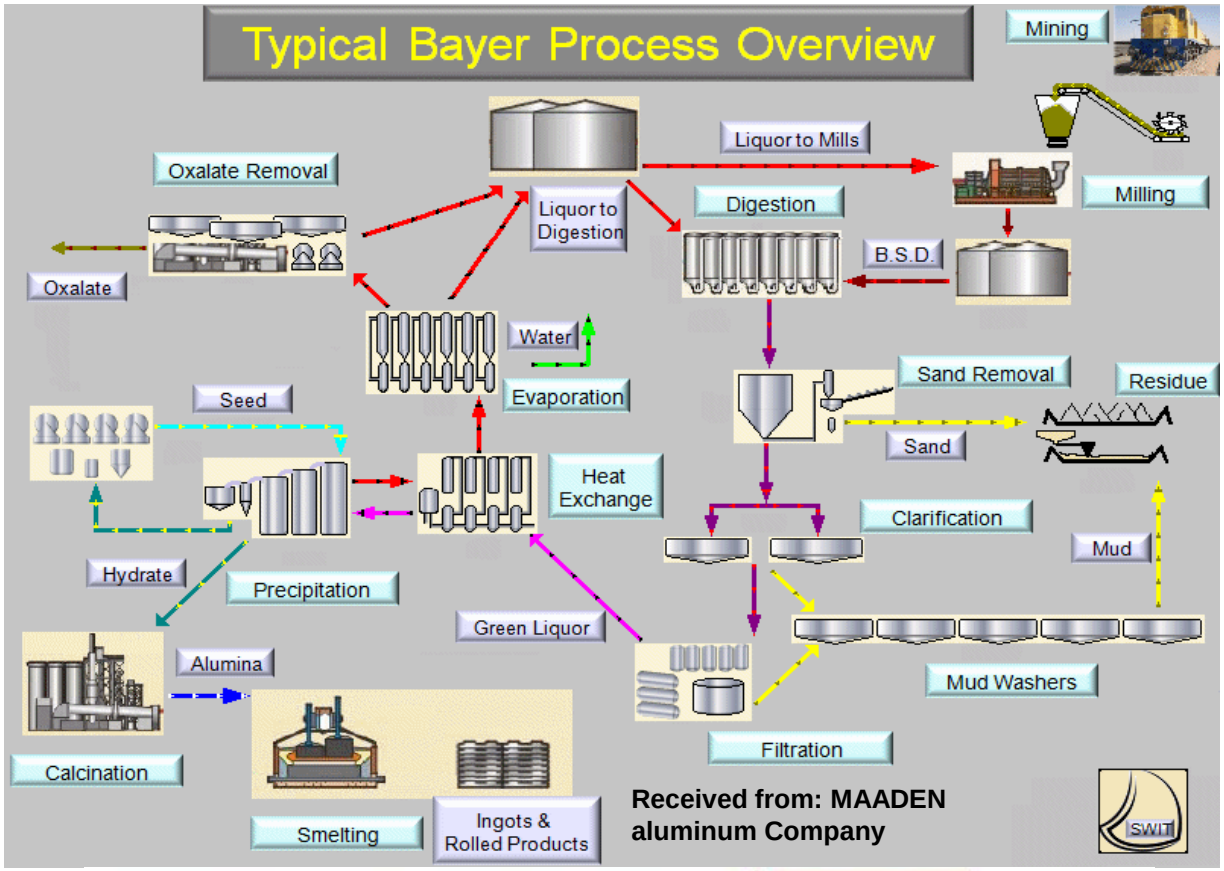
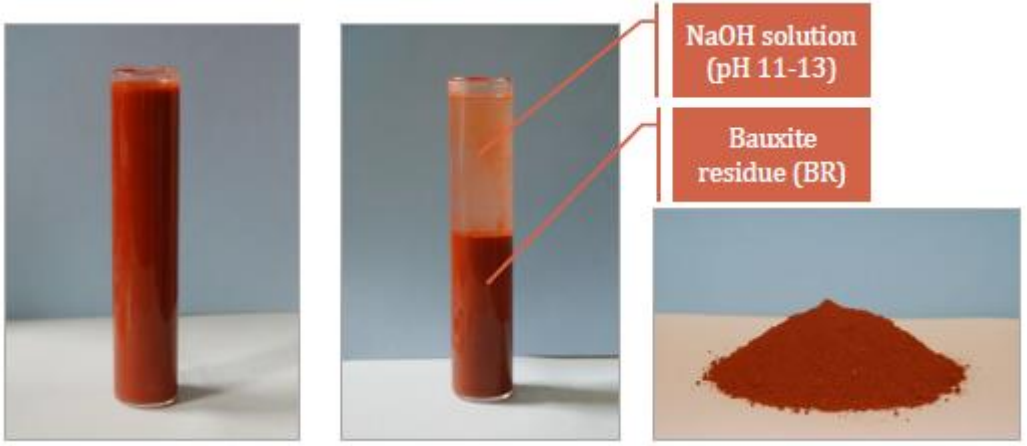
What is Red Mud

- Red mud is waste product of aluminum refinery
- It is toxic with high PH value
- It is finely powdered muds which badly affect the air, land and water environment of adjacent area
- its major constituents are CaO, Al_2O_3, SiO_2, Na_2O, TiO_2 and Fe_2O_3, with little amounts of Ga,V, Sr, Zr,Y, Th, U and rare earth elements as trace constituents.
- 1.0–1.5 ton of red mud is produced to produce of 1 ton of alumina





Motivation

- Waste is waste if we waste it. Otherwise it is a resource.
- Red Mud: Potential secondary raw materials
- Possible use of red mud as:
  Construction materials (cement, bricks, roofing tiles, glass ceramics), coagulant, absorbent and catalysts, paints, geopolymer, coatings, extraction of iron, titanium, aluminum, material for waste water treatment to remove toxic heavy metals

Objective

- **The objective of this research is to utilize the waste red mud as valuable products.**
- **The research was conducted in two steps:**

  Step 1: Characterization of Saudi Red mud

  Step 2: Prepare ceramic coating from modified red mud

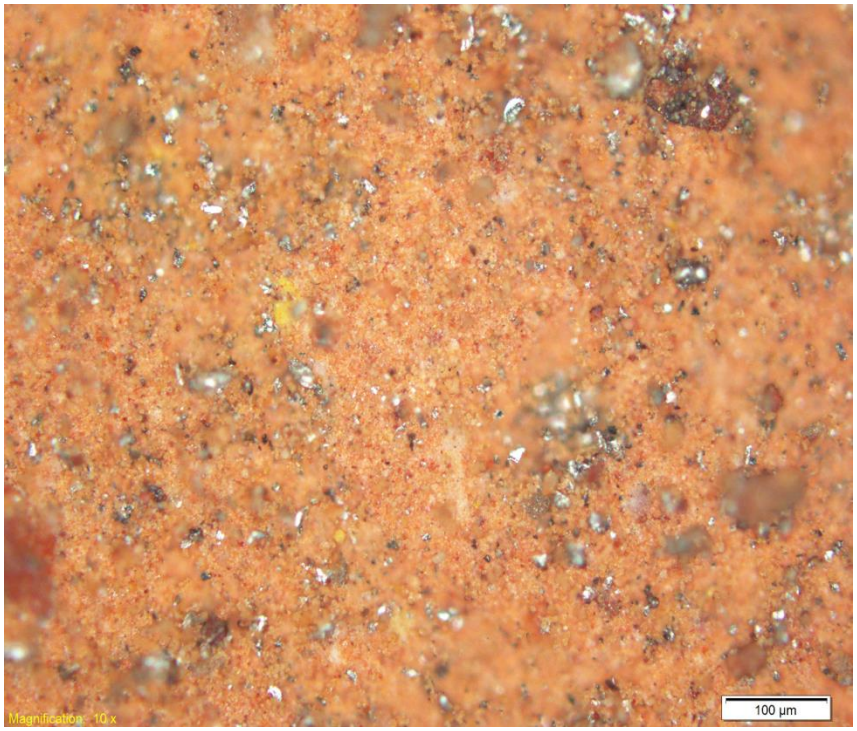
Research Methodology of characterization of Saudi Red mud

- Collection of Saudi Red mud from Maaden Aluminum Company
- Measurement of PH value of Saudi Red mud
- Neutralization of Saudi red mud by reducing PH value
- Removal of volatile materials
- Analysis of chemical compositions by X-ray Florescence analysis
- Analysis of crystals structure of Saudi red mud by using X-ray diffraction
- Analysis of phases by using Scanning Electron Microscope and EDX analysis
- Conduct thermal analysis by using TGA (Thermo gravimetric analysis)

Removing volatile materials

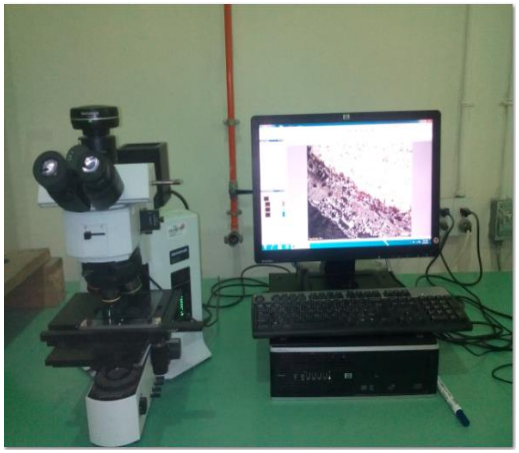
Volatile materials from red mud was removed by heating inside the furnace.

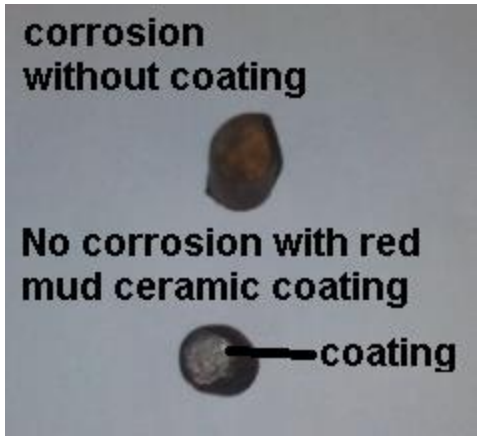
Microstructure of original red mud



Microstructure after sintering

Experimental setup





Red mud neutralization

- ❖ PH value of Saudi Red mud slurry was found 12.
- ❖ PH value should be less than 9 with optimum value of 8.5 -8.9
- ❖ Red mud can be neutralized by:
  - Acid Neutralization
  - CO_2 treatment
  - Sea water neutralization
  - Bioleaching
  - Sintering

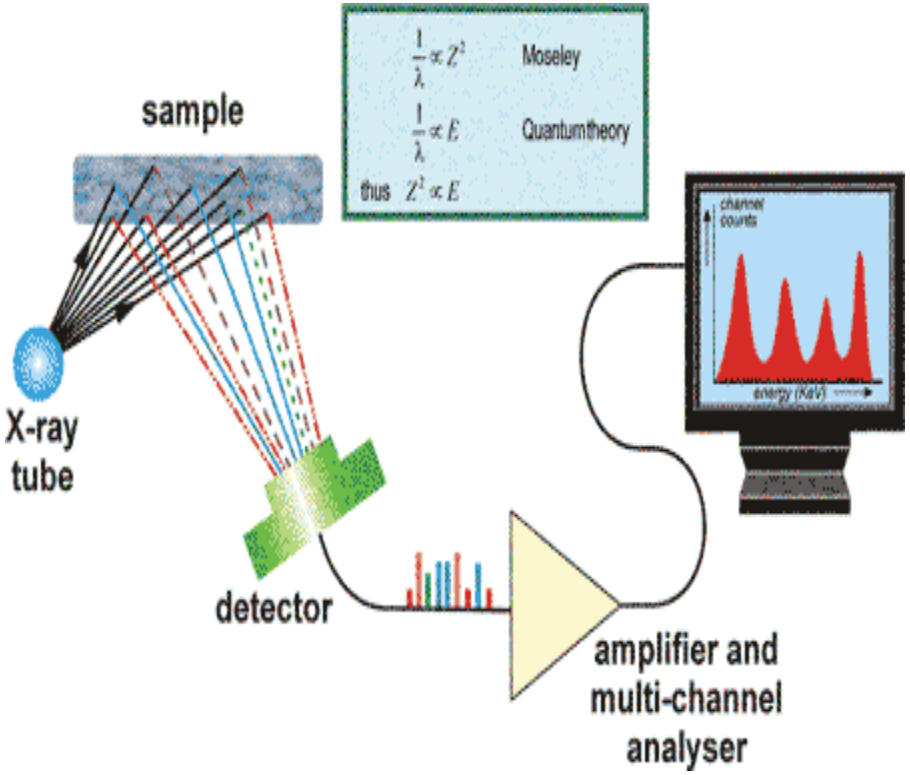
Red mud neutralization

Red mud	PH value
Red mud slurry	13.0
Neutralized red mud	8.5

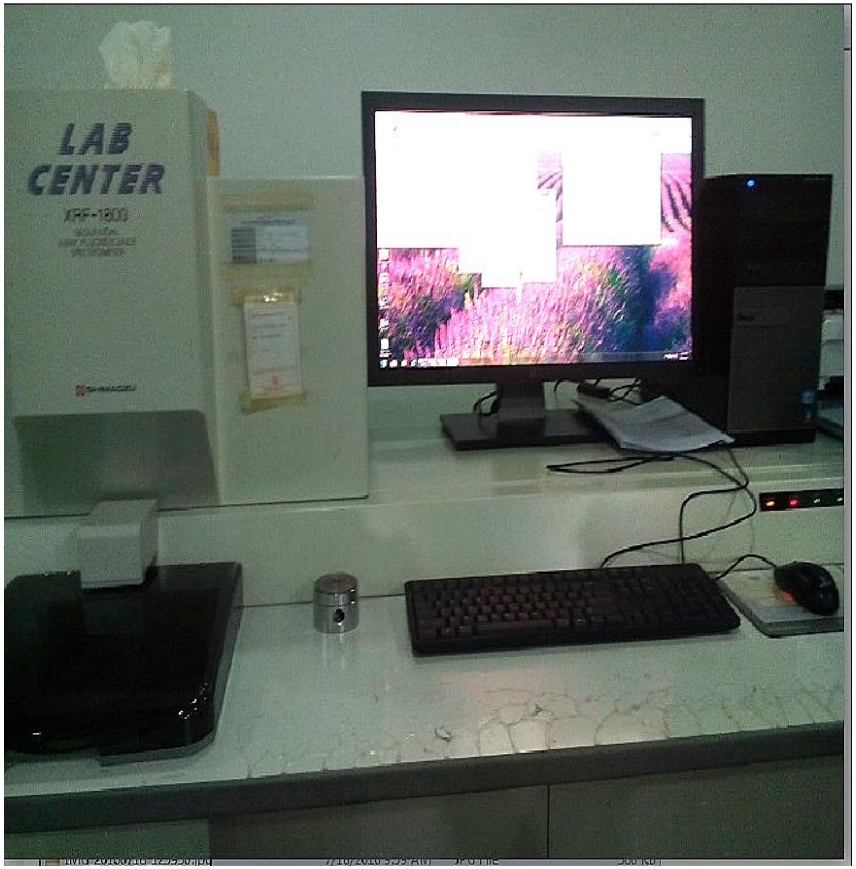
- **The PH value was reduced in this research from 13 to 8.5 before preparing red mud powder as coating materials**

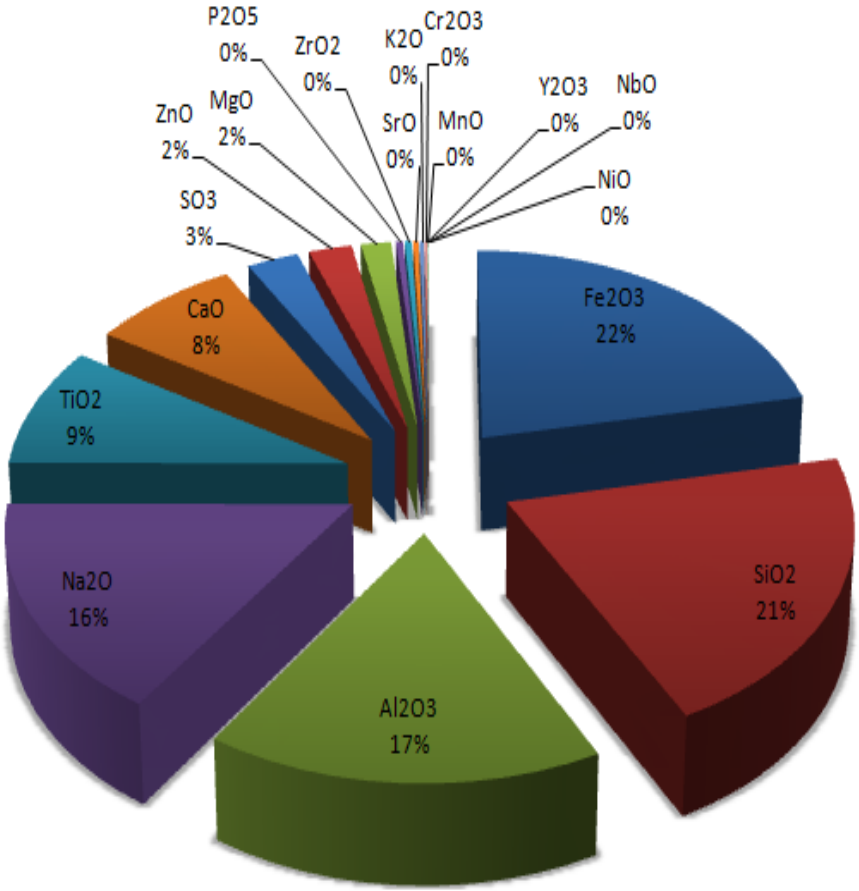
XRF analysis of Saudi Red Mud

- In XRF analysis the red mud pellet is placed near x-ray tube and bombarded with x-rays
- The primary x-rays causes the sample to emit secondary fluorescent x-ray which is then analyzed by a spectrometer.
- As each element in red mud has a set of characteristic x-rays of specific wavelength, chemical analysis for a particular element is accomplished by analyzing the fluorescent spectra.
- X-ray Fluorescence Spectroscopy (model: Lab center XRF-1800, Shimadzu-japan) was used to analyze chemical composition of dried red mud.



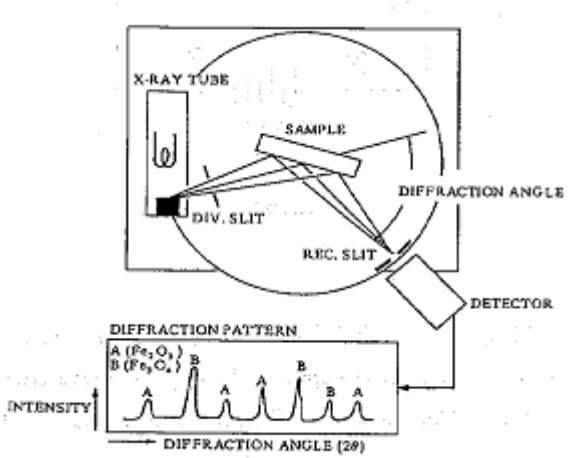
XRF analysis of Saudi Red Mud





XRD analysis of Saudi Red Mud

- **In XRD analysis, x-rays which are incident on powdered red mud sample were reflected by the sample and were received by the x-ray detector to produce the reflection spectrum . This reflection spectrum are named as x-ray diffraction pattern.**
- **The x-ray diffraction pattern is characteristic of the substance and each substance in a mixture of some substances produces its pattern independently of the others**
- **Therefore the chemical analysis for a particular substance is accomplished by identification of the pattern of that substance**

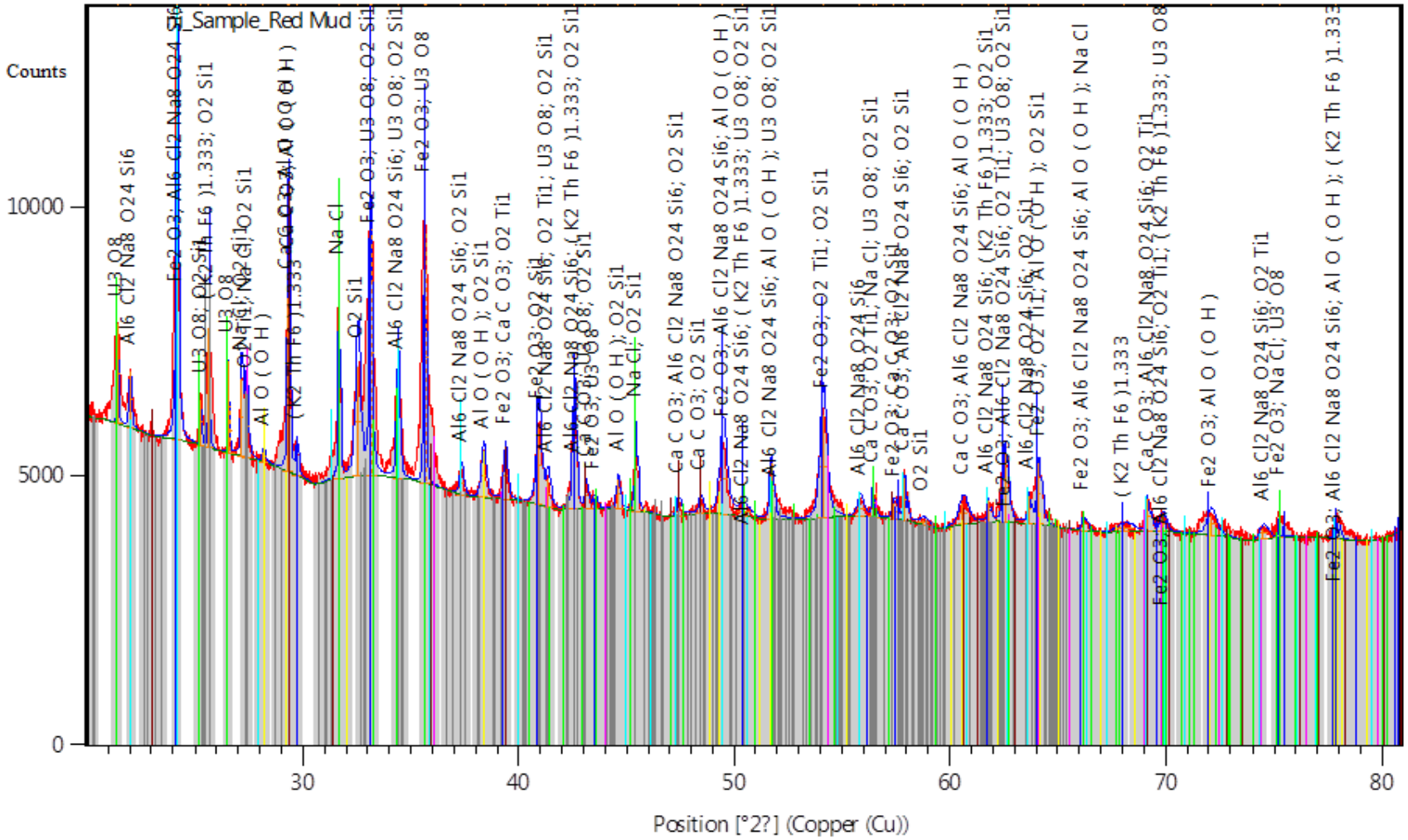


- XRD measure the average spacing between layers or rows of atoms
- Find crystal structure of unknown material
- Determine the orientation of a single crystal or grain

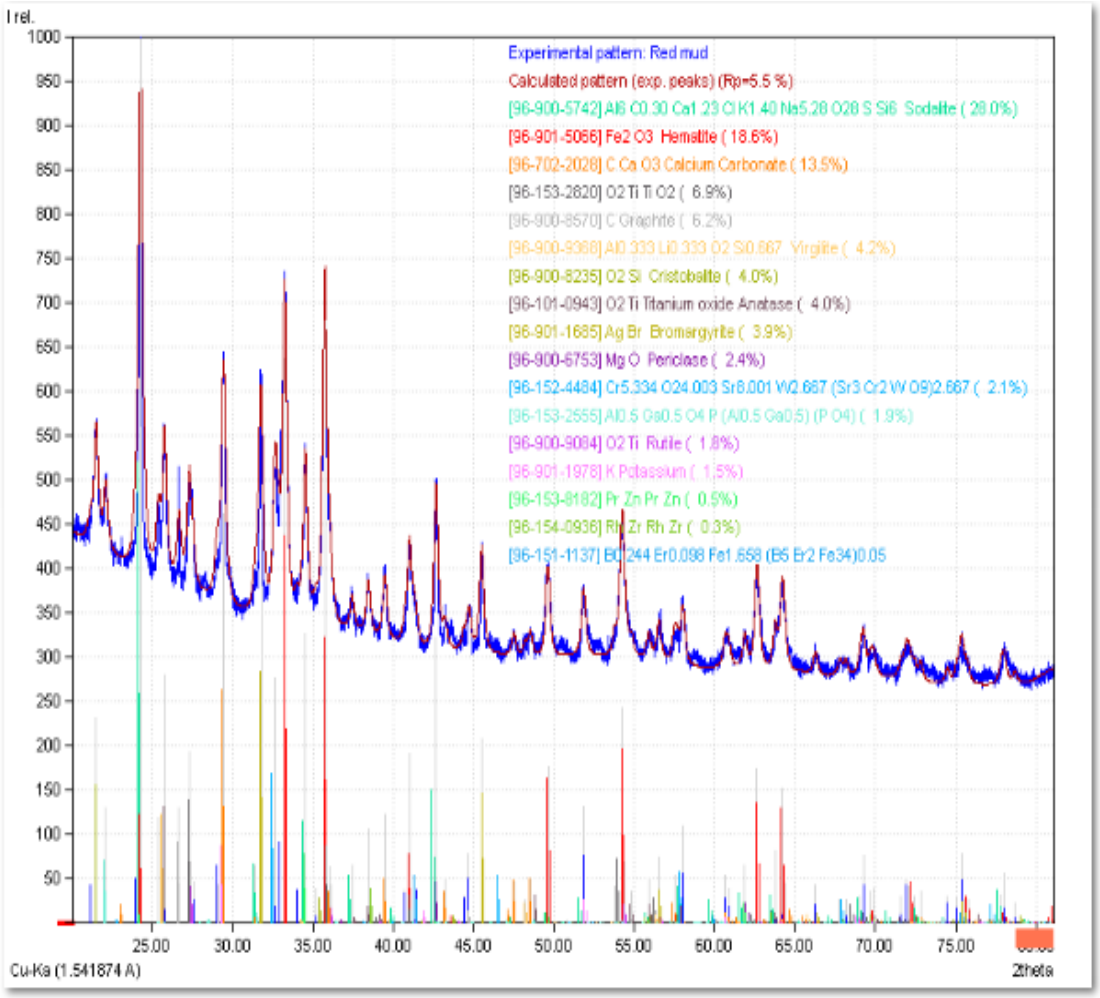
XRD analysis of Saudi Red Mud

Compound Name	Chemical Formula	Score	SemiQuant [%]	Display Color
Iron Oxide	Fe2 O3	55	22	Blue
Calcium Carbonate	Ca C O3	36	11	Maroon
Sodalite	Al6 Cl2 Na8 O24 Si6	47	31	Aqua
Rutile	O2 Ti1	25	4	Fuchsia
Aluminum Oxide Hydroxide	Al O (O H)	16	6	Yellow
Sodium Chloride	Na Cl	47	8	Lime
Potassium Thorium Fluoride	(K2 Th F6)1.333	38	3	Blue
Uranium Oxide	U3 O8	23	2	Lime
Zeolite	O2 Si1	33	13	Gray

XRD analysis of Saudi Red mud



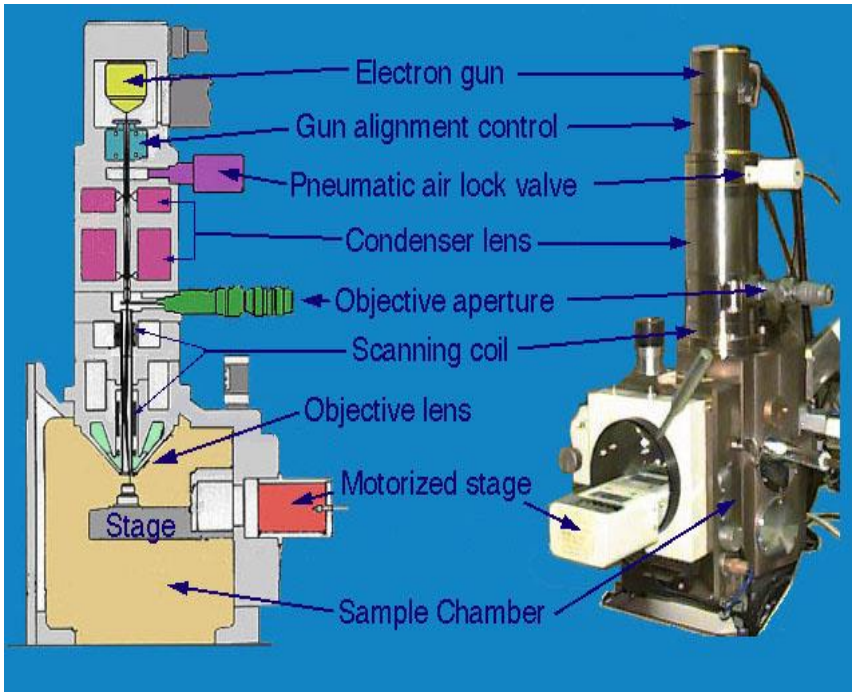
Red mud data analyzed by Match software



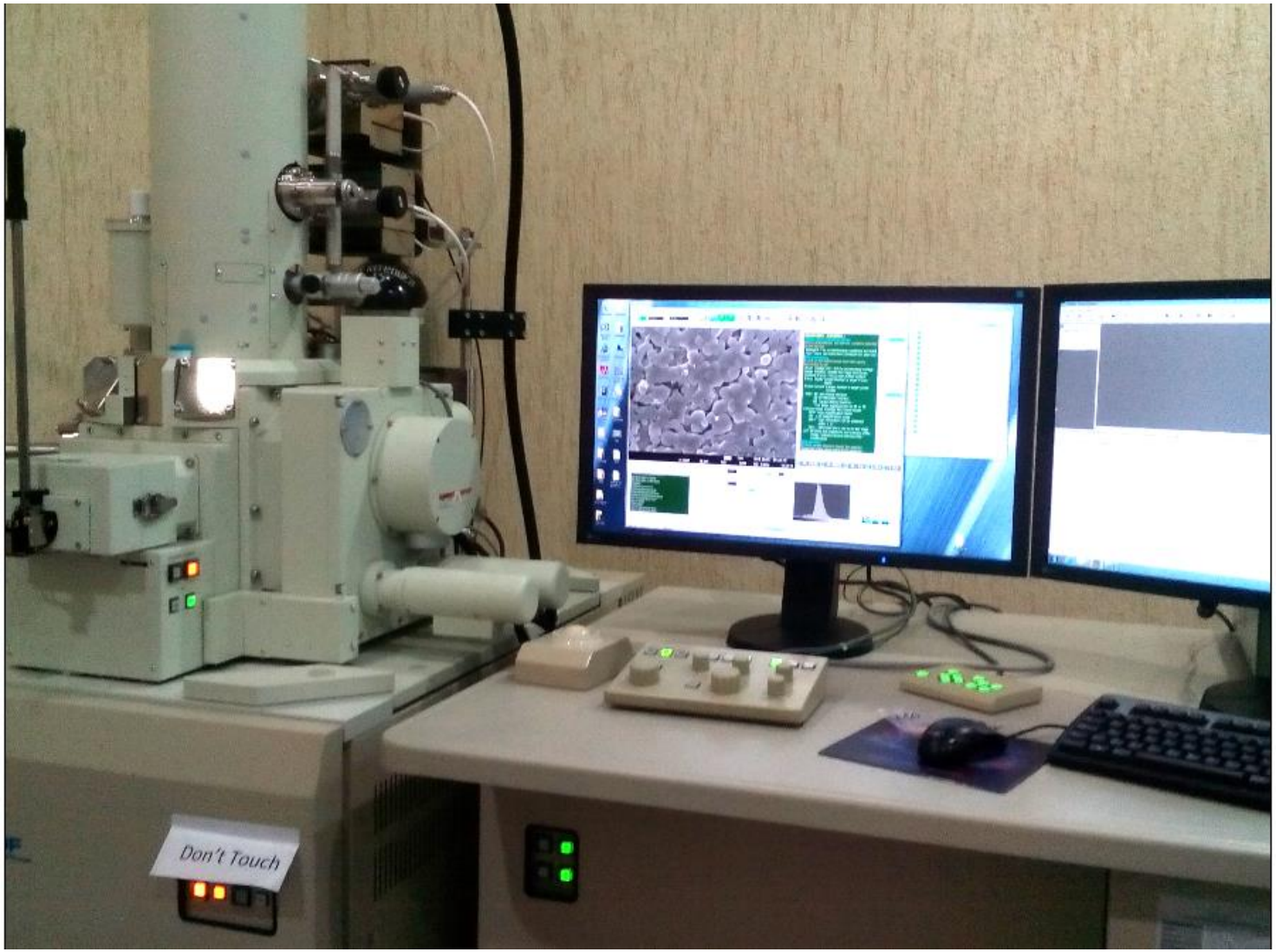
Al6 C0.30 Ca1.23 Cl K1.40 Na5.28 O28 S Si6;	(Sodalite);	28.0
Fe2 O3;	Hematite;	18.6
C Ca O3;	Calcium Carbonate;	13.5
O2 Ti;	Ti O2;	6.9
C;	Graphite;	6.2
Al0.333 Li0.333 O2 Si0.667;	Virgilite;	4.2
O2 Si;	Cristobalite;	4.0
O2 Ti;	Titanium oxide Anatase;	4.0
Ag Br;	Bromargyrite;	3.9
Mg O;	Periclase;	2.4
Cr5.334 O24.003 Sr8.001 W2.667;	(Sr3 Cr2 W O9)	2.667;2.1
Al0.5 Ga0.5 O4 P;	(Al0.5 Ga0.5) (P O4);	1.9
O2 Ti;	Rutile;	1.8
K;	Potassium;	1.5
Pr Zn;	Pr Zn;	0.5
Rh Zr;	Rh Zr;	0.3

Scanning Electron Microscope

- **SEM is a microscope that uses electrons rather than light to form an image**
- **The combination of higher magnification, larger depth of field, greater resolution and compositional and crystallographic information makes the SEM one of the most important instrument for research and industries.**
- **SEM generates a beam of electrons in a vacuum. The electron beam is collimated by electromagnetic condenser lenses, focused by an objective lens, and scanned across the surface of the sample by scanning coils. The primary imaging method is by collecting secondary electrons that are released by the sample. By correleting the sample scan position with the resulting signal, an image can be formed.**

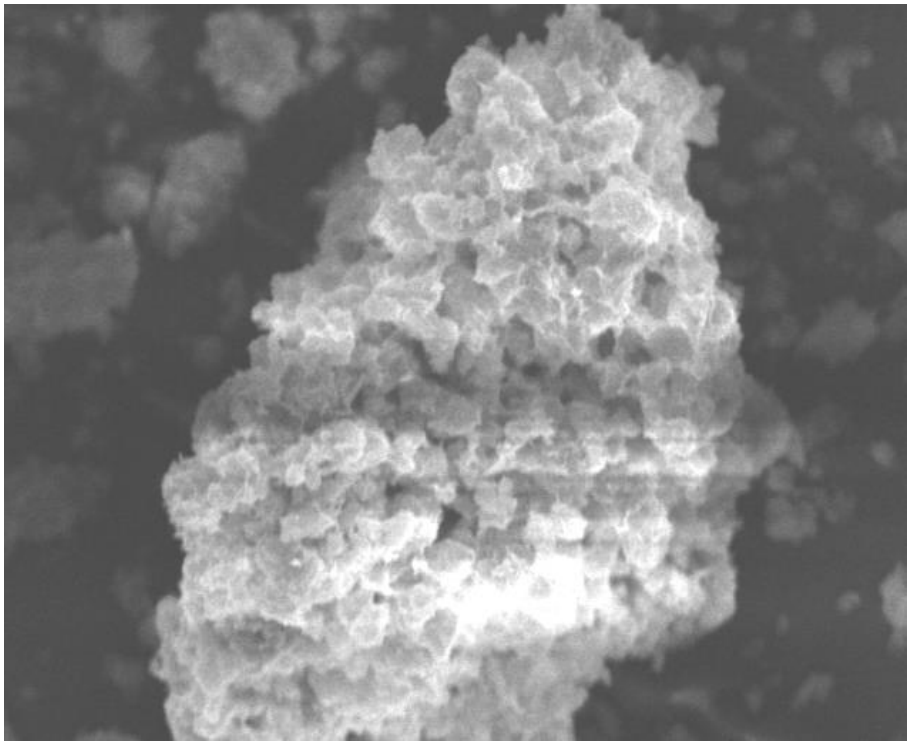


Scanning Electron Microscope

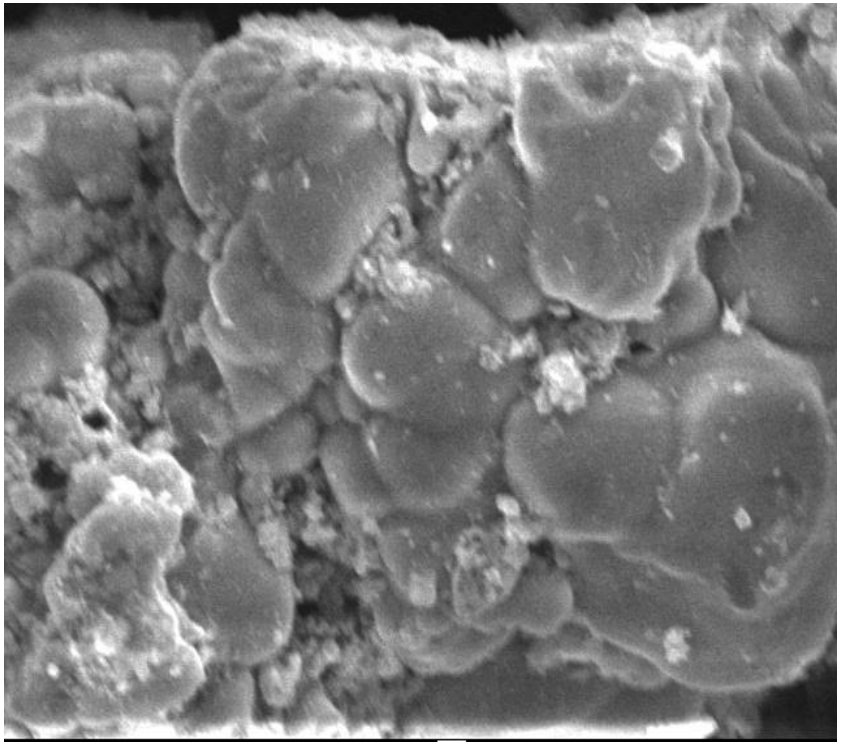


SEM analysis of Saudi Red mud

Smaller particles



Larger particles

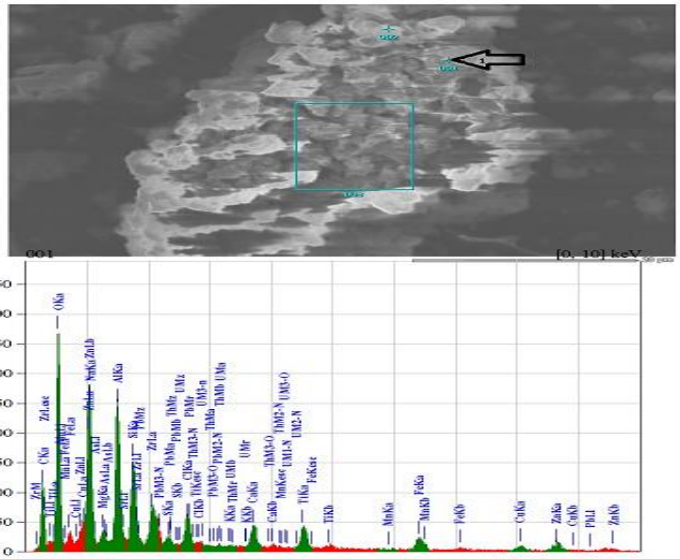


EDX analysis

Elements	Smaller particles	Larger particles
C	35.15%	6.72%
O	18.95%	16.41%
Na	8.26%	0.53%
Al	9.08%	0.87%
Si	5.66%	0.49%
Fe	7.10%	68.58%

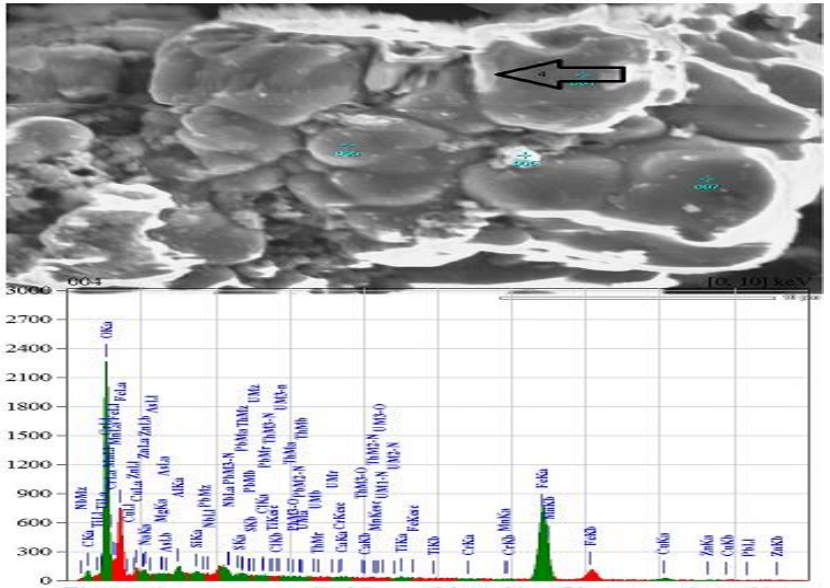
EDX analysis of Saudi Red mud

EDX of smallar grain



Element	(keV)	Mass%	Sigma	Atom%
C K	0.277	35.23	0.40	57.60
O K	0.525	14.51	0.16	17.81
Na K	1.041	6.28	0.14	5.36
Mg K *	1.253	0.65	0.05	0.53
Al K	1.486	6.84	0.12	4.98
Si K *	1.739	4.45	0.11	3.11
S K *	2.307	0.60	0.04	0.37
Cl K *	2.621	2.11	0.07	1.17
K K *	3.312	0.14	0.04	0.07
Ca K *	3.690	2.34	0.09	1.15
Ti K *	4.508	3.69	0.12	1.51
Mn K *	5.894	0.13	0.07	0.05
Fe K *	6.398	3.87	0.18	1.36
Cu K *	8.040	3.20	0.26	0.99
Zn K *	8.630	8.81	0.49	2.65
As L *				
Sr L *	1.806	0.99	0.21	0.22
Zr L *	2.042	4.19	0.17	0.90
Pb M *	2.342	1.67	0.16	0.16
Th M *	2.991	0.22	0.12	0.02
U M *	3.164	0.06	0.28	0.00
Total		100.00		100.00

EDX of larger grain

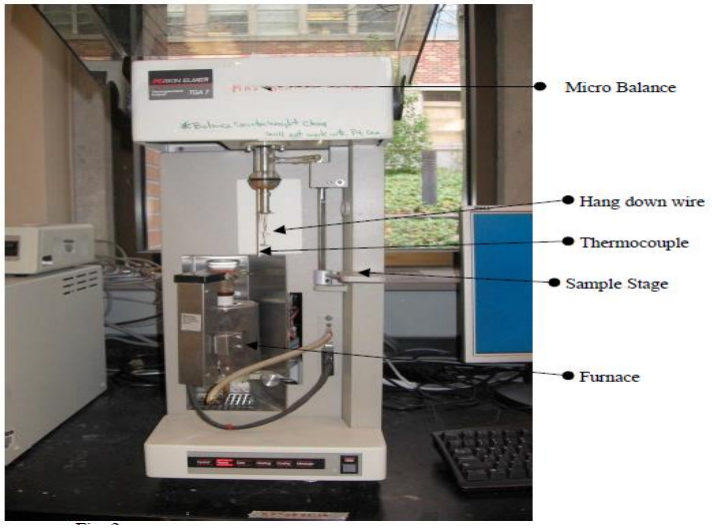


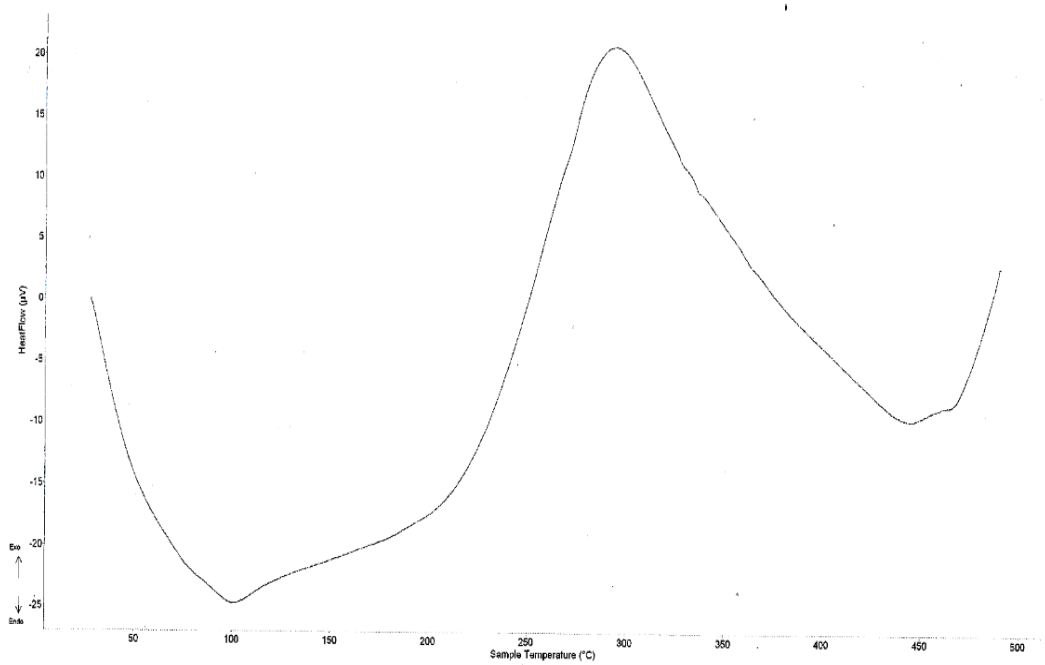
Element	(keV)	Mass%	Sigma	Atom%
C K	0.277	7.68	0.19	20.91
O K	0.525	16.31	0.12	33.37
Na K	1.041	0.91	0.12	1.30
Mg K	1.253	0.08	0.06	0.10
Al K	1.486	1.43	0.09	1.74
Si K	1.739	0.45	0.07	0.53
S K	2.307	0.31	0.04	0.32
Cl K	2.621	0.02	0.04	0.02
Ca K	3.690	0.11	0.06	0.09
Ti K	4.508	0.38	0.07	0.26
Cr K	5.411	0.08	0.07	0.05
Mn K	5.894	0.70	0.11	0.42
Fe K	6.398	65.91	0.78	38.62
Cu K *	8.040	3.73	0.33	1.92
Zn K	8.630	0.19	0.24	0.09
As L				
Nb L				
Pb M	2.342	1.71	0.20	0.27
Th M				
U M				
Total		100.00		100.00

Thermo gravimetric analysis

•TGA is commonly used to determine selected characteristics of materials that exhibit either mass loss or gain due to decomposition, oxidation, or loss of volatiles (such as moisture).

•The endothermic pick is found at 100 ^{0} C because of the heat absorbed by water evaporation due to the removal of adsorbed water from red mud. At 300 ^{0} C, the heat is released having an exothermal pick, which is likely due to oxidation of organic matters absorbed in red mud. The hydrothermal crystallization of amorphous titanium oxide at 300-600 ^{0} C might occur. The experiment was not conducted above 600 ^{0} C because of lack of higher temperature instrument.





Research Methodology to prepare ceramic coating

- Preparation of coating powder
- Collection of metal substrate
- Cleaning the metal substrate
- Application of the red mud coating on metal substrate
- Drying of the red mud coating
- Application of heat by flame
- Hardness measurement of coating
- Microstructure observation of coating
- Corrosion test

Corrosion of water pipe

- Pipes made of metal, concrete and polymer are used to transport normal water and waste water.
- The pipes used at high pressure pipelines are mostly made of carbon steels.
- Carbon steel without coating deteriorates by corrosion.
- The water and oxygen are responsible for external corrosion of carbon steel pipe.

  $Fe \rightarrow Fe_2+ + 2e-$

  $O_2 + 2H_2O + 2e- \rightarrow Fe(OH)_2$

Corrosion of water pipe

- The presence of water and oxygen can be prevented by applying coating on pipe surface
- Cathodic protection along with coating is the best corrosion protection system for under ground pipe lines .
- Common pipe coatings for exterior surface of pipe are: Bituminus enamels; Zinc/bituminus coating; Fusion bonded epoxy coating; cement mortar; ceramic coating

Ceramic coating

CERAMIC COATING → **Properties of ceramics**

- Corrosion/oxidation resistance
- Thermal
- Electrical
- Optical
- Magnetic
- Wear-resistant

CERAMIC COATINGS PROCESS

- Sol-gel
- Vapour phase: PVD and CVD
- Thermal Spray Process: LVOF, HVOF, VPS and APS
- Laser
- *Electrophoretic deposition (EPD)*

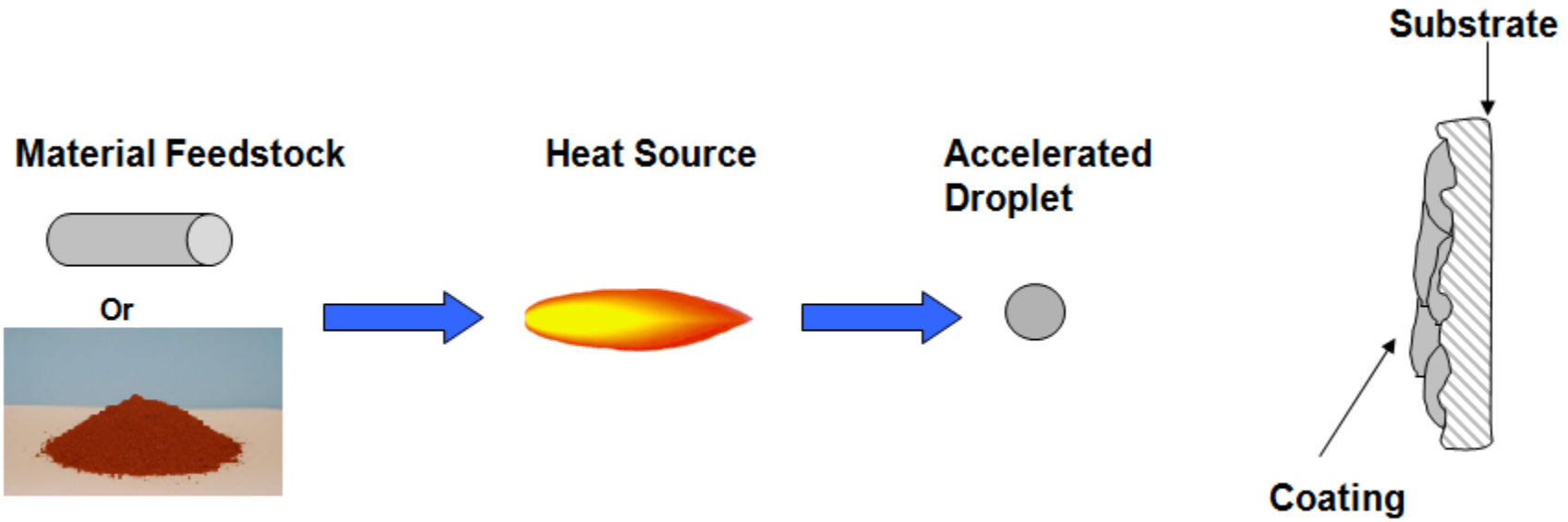
Received from:

kera-coat CERAMIC COATINGS

Electrophoretic deposition is a colloidal processing technique to deposit thin films and coatings on substrates. After EPD, the obtained coating, which is in fact still a powder compact, has to be densified by a **heat treatment**.

Red Mud coating by Thermal Spray

• Plasma spray is the best method to apply red mud coating on metal substrate.
• In this experiment flame was used because of lack of thermal spray machine in our lab.



- Ceramic coating by using thermal spray method produce strong mechanical bond with substrate.

- The characteristics of thermal spray red mud ceramic coating are:

1. There are metal oxide (Al_2O_3, Fe_2O_3, TiO_2 etc) stringers and porosity in the coatings

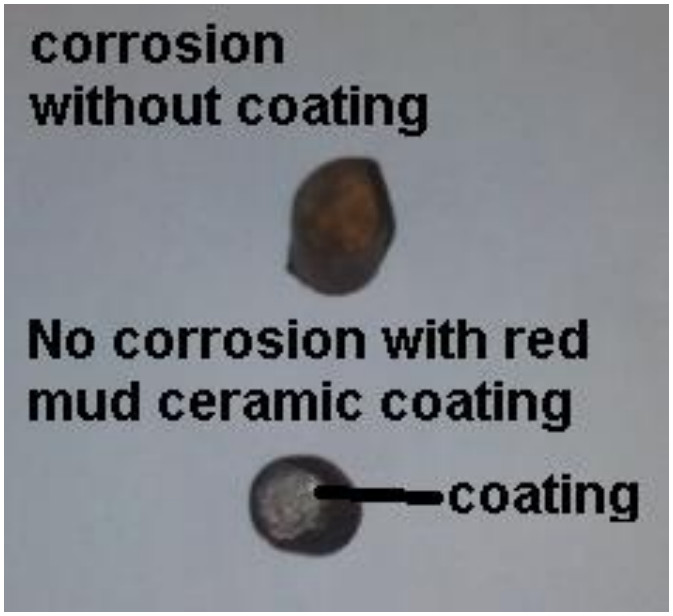
2. Layered effect is created in the coating structure because of presence of metal particles

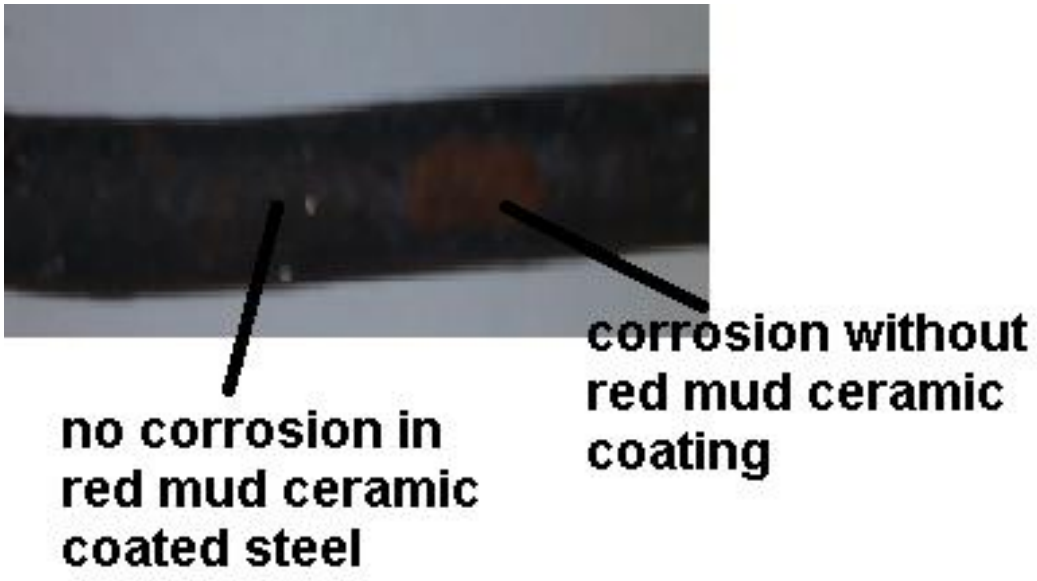
3. Thermal sprayed coatings have unique crystalline structures due to the rapid cooling of the metal particles as they adhere to the substrates

Hardness Test and Corrosion Test

- The hardness of carbon steel substrate was found 160 HV
- The hardness of ceramic coating made by Saudi red mud was found 662 HV which is 4.14 times higher than steel substrate
- Corrosion test was conducted with salt water and sea water from Al Nakheel beach for 144 hours.

Hardness Test and Corrosion Test

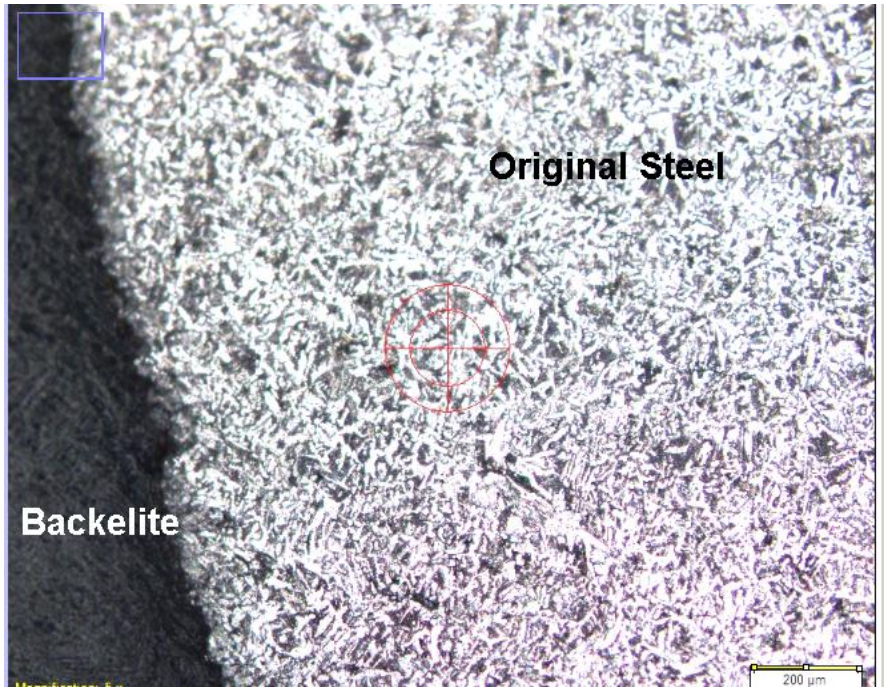




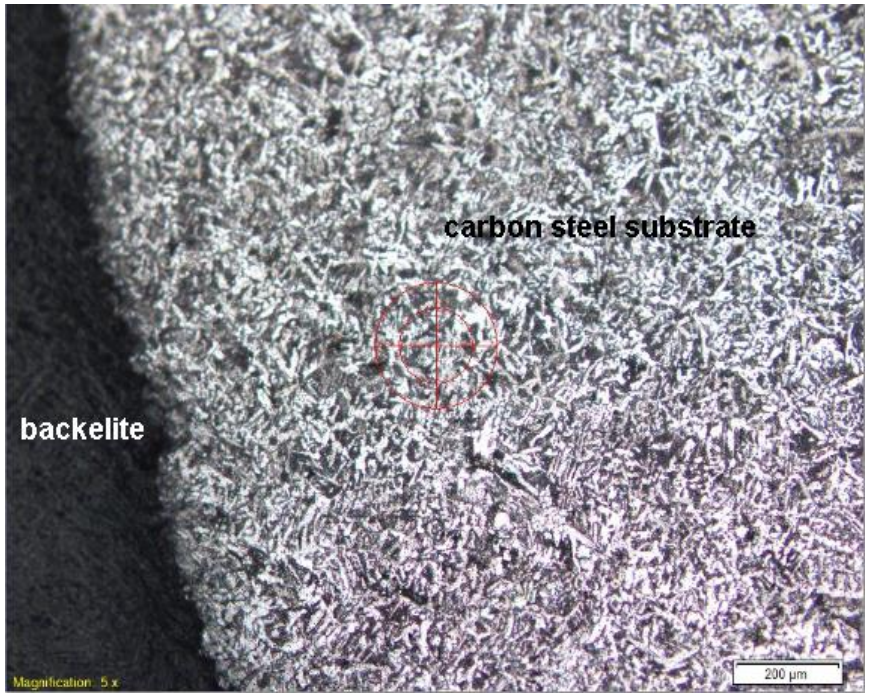
It was found that the red mud ceramic coated area was protected against corrosion compare to the bare area of carbon steel substrate.

Microstructure observation of Red mud ceramic coating

Hypoeutectoid carbon steel substrate X 50

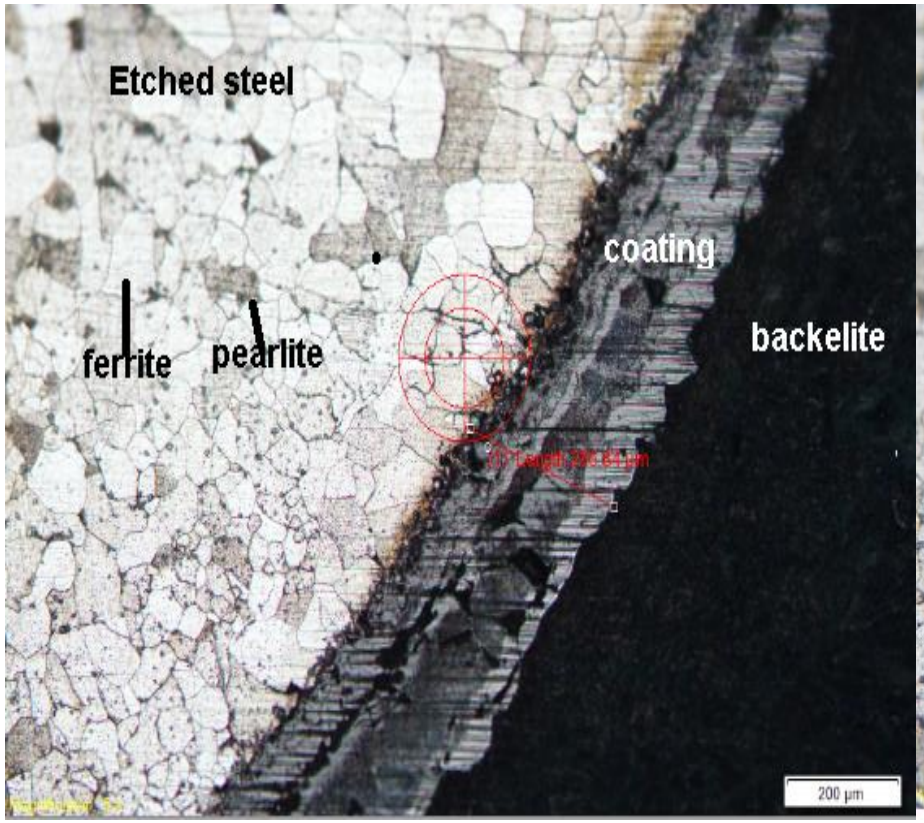


Hypoeutectoid carbon steel substrate X 100

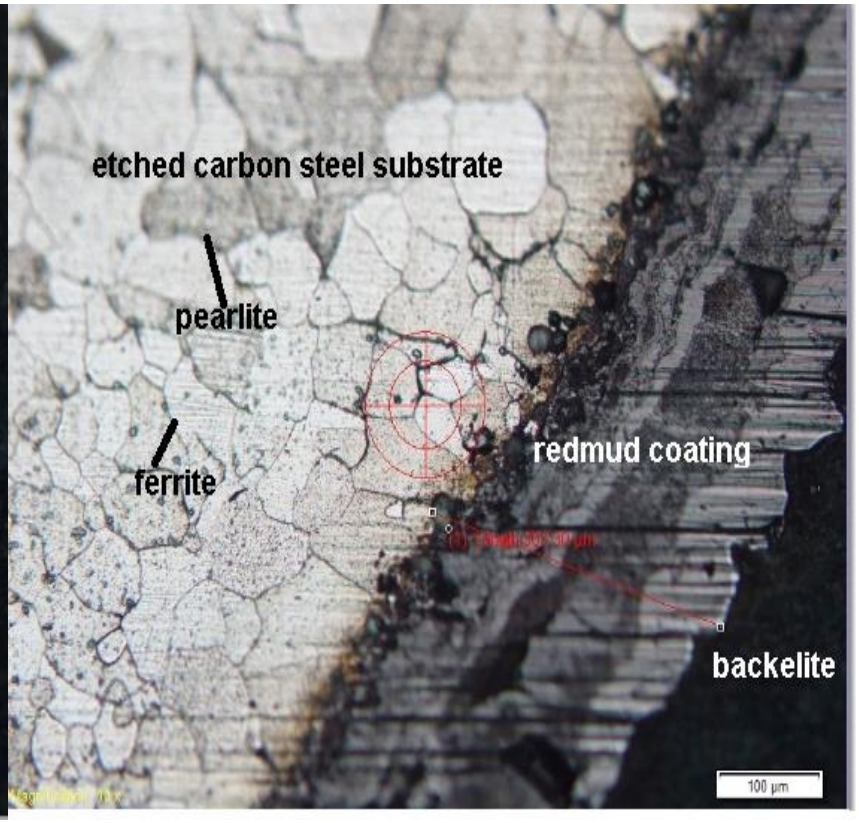


Microstructure observation of ceramic coating

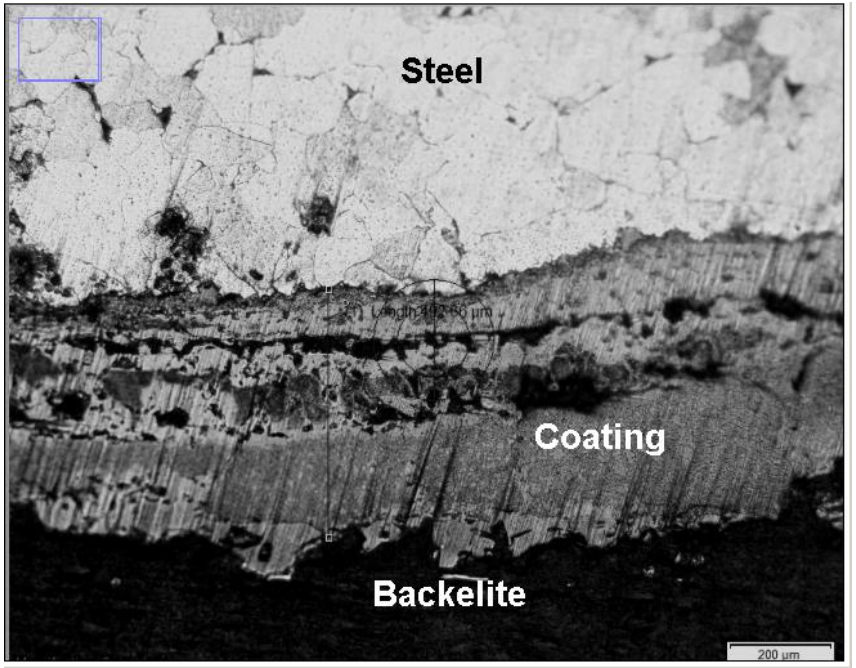
Red mud ceramic coating on carbon steel
X 100

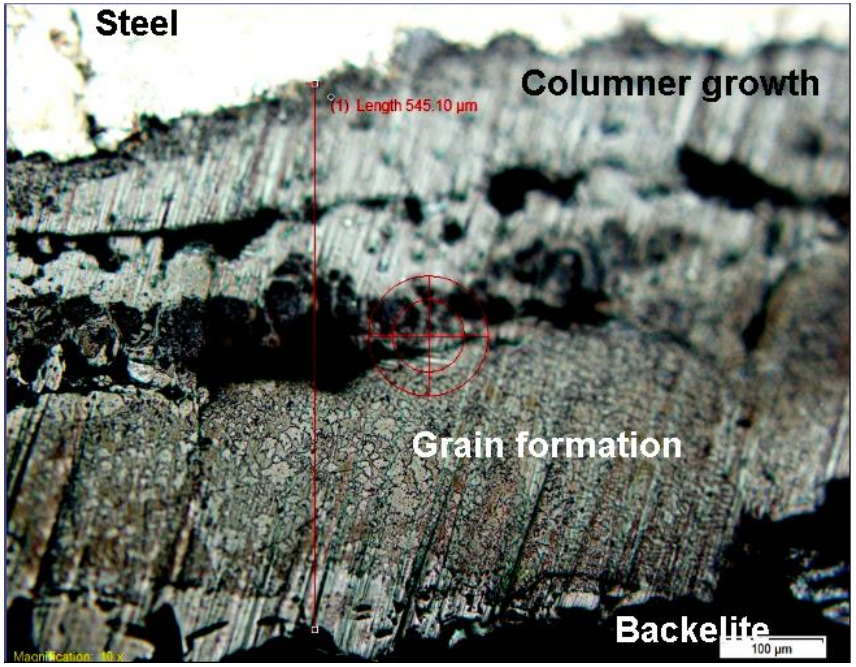


Red mud ceramic coating on carbon steel
X 200



Columnar grain of red mud coating on steel substrate

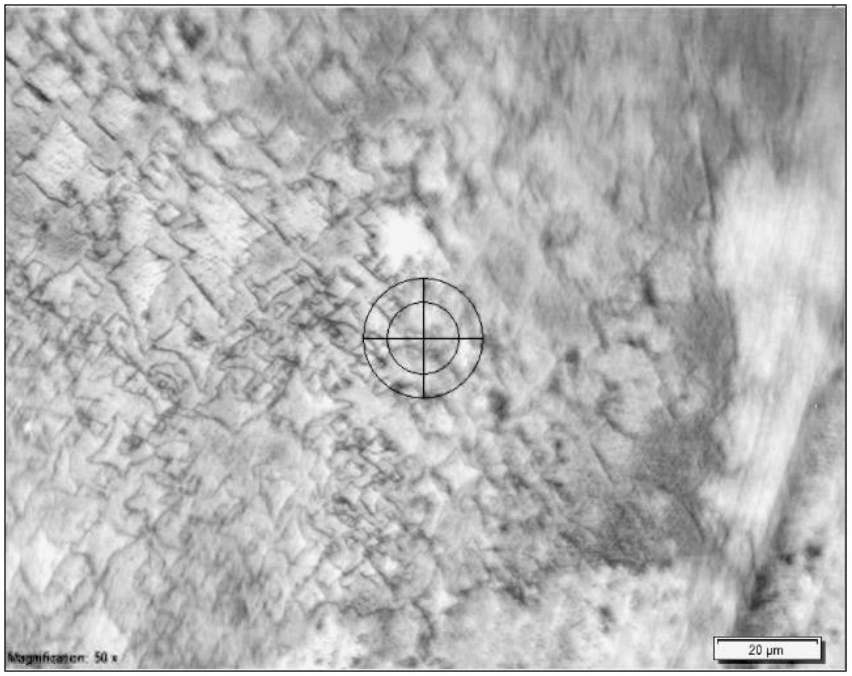




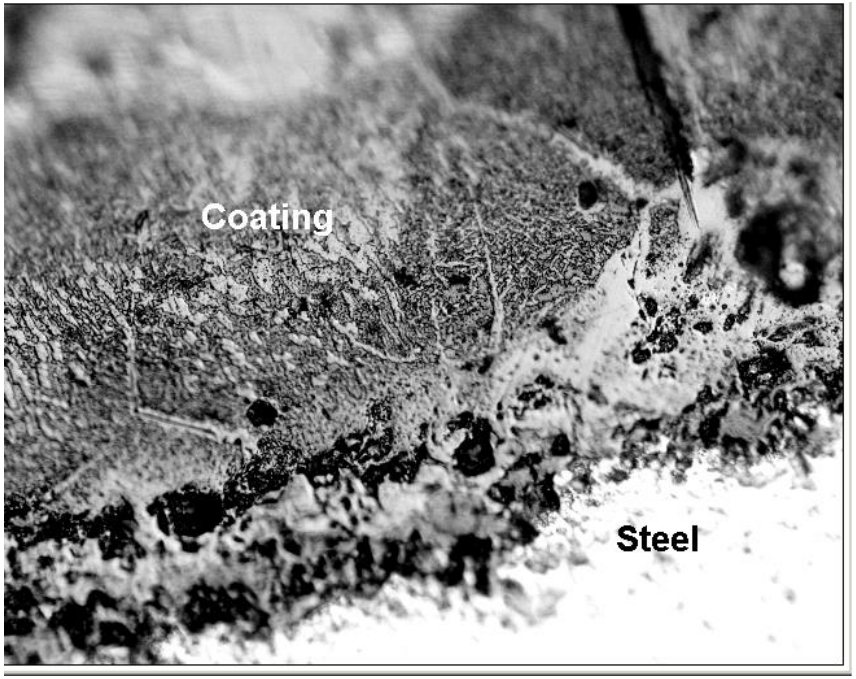
Different phases of red mud coating

Smaller grains of coating (A) x500 and porosity in coating (B) x 500

(A)

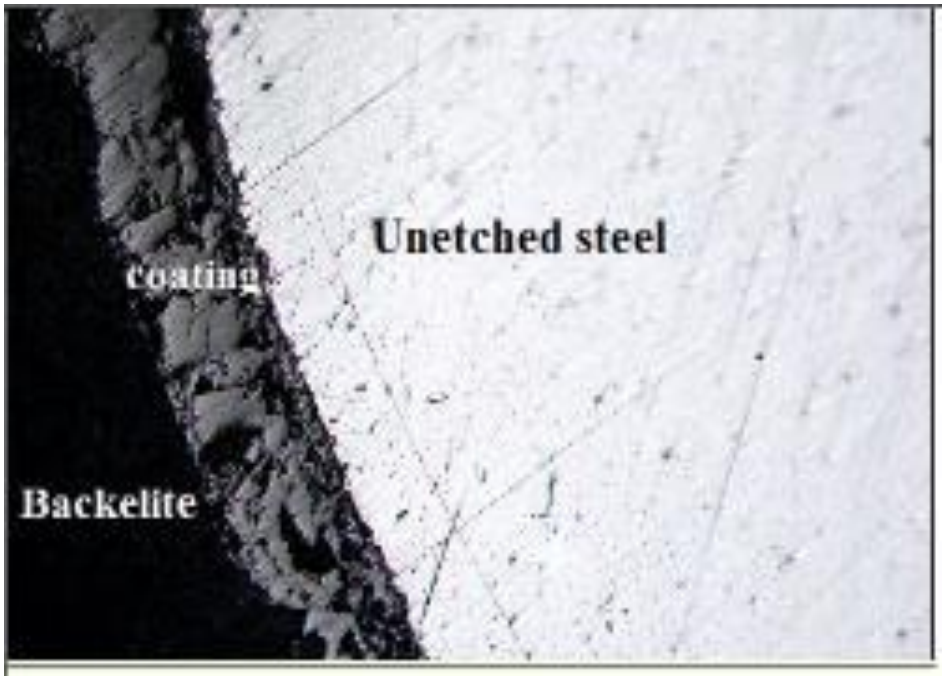


(B)

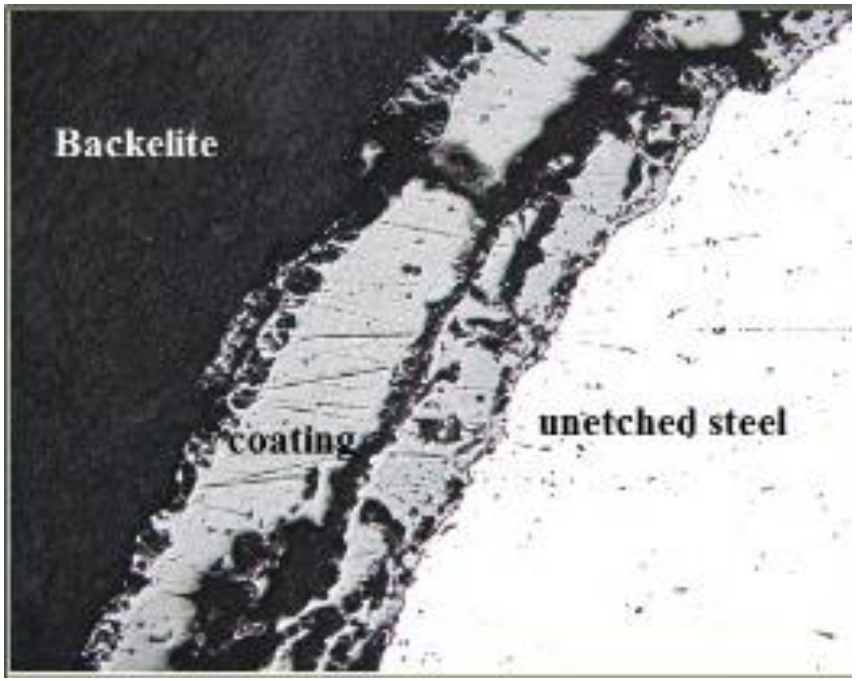


Microstructure of coating without etching

x50

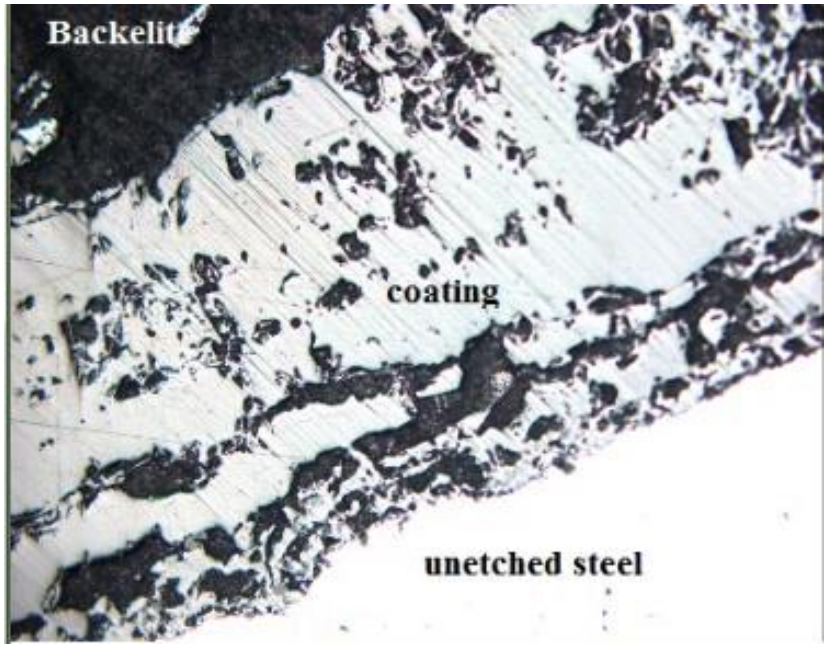


x100

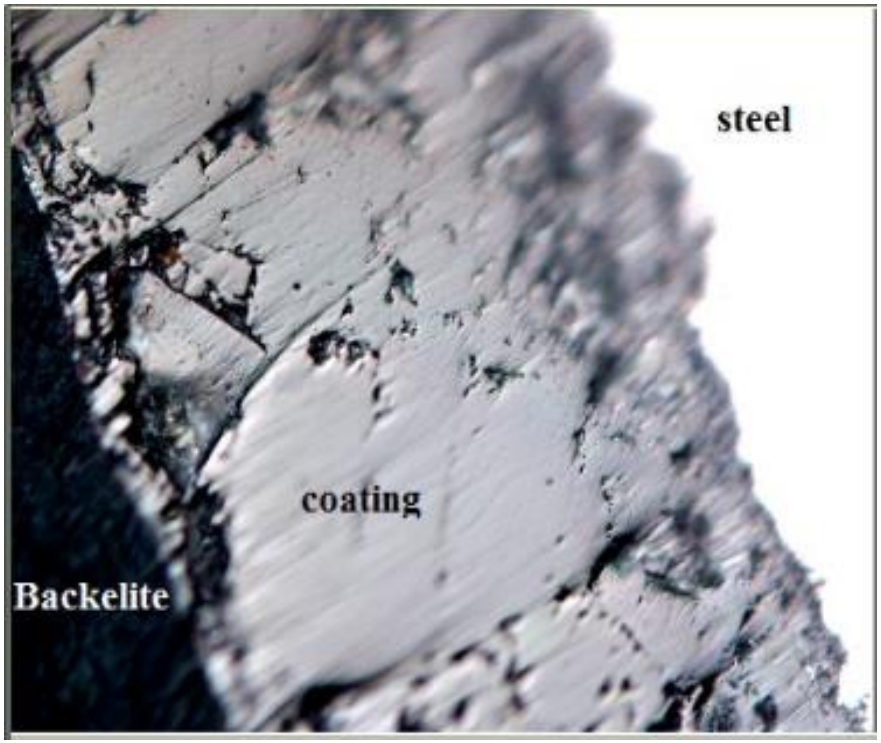


Microstructure of coating without etching

x200

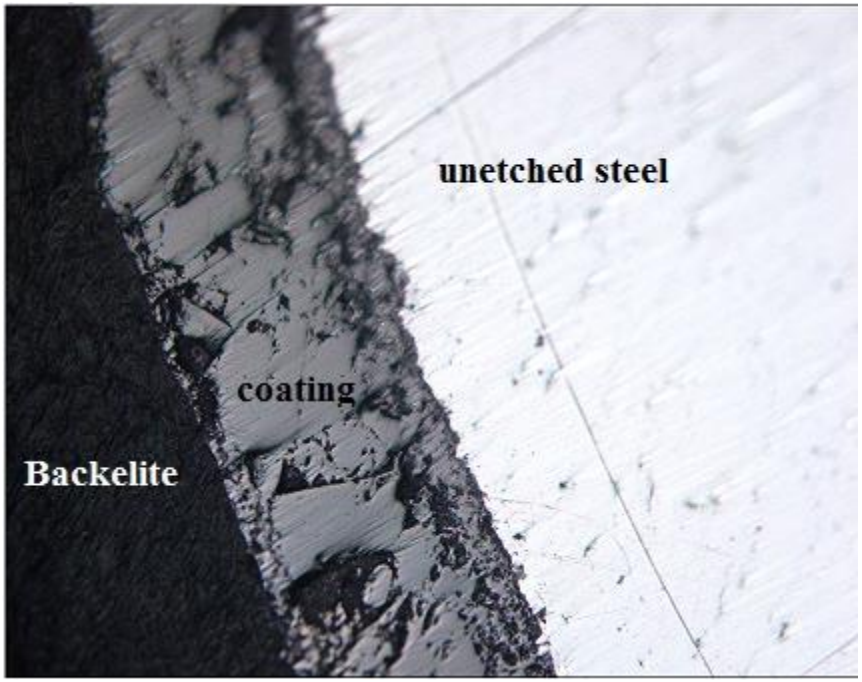


x500

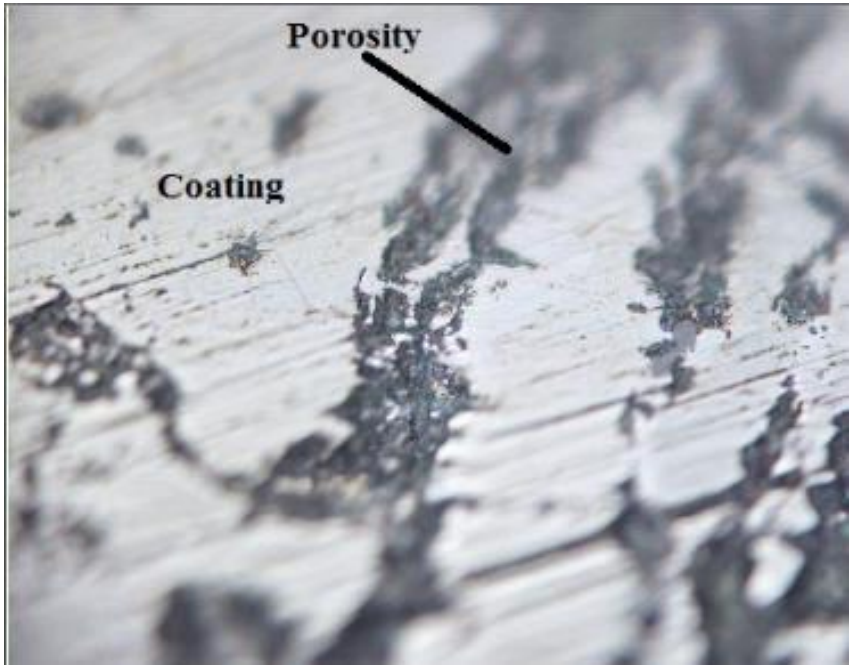


Microstructure of coating without etching

x200

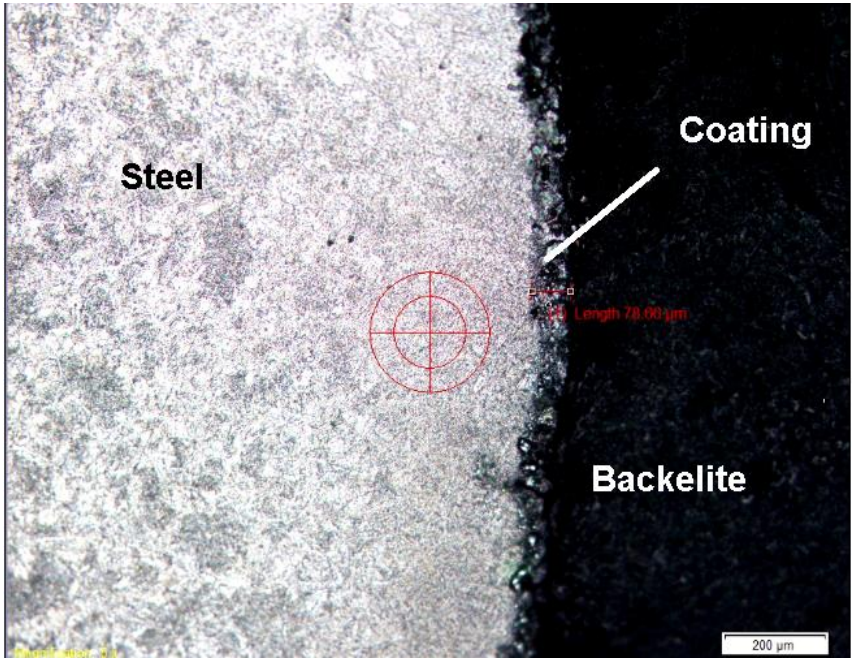


x1000

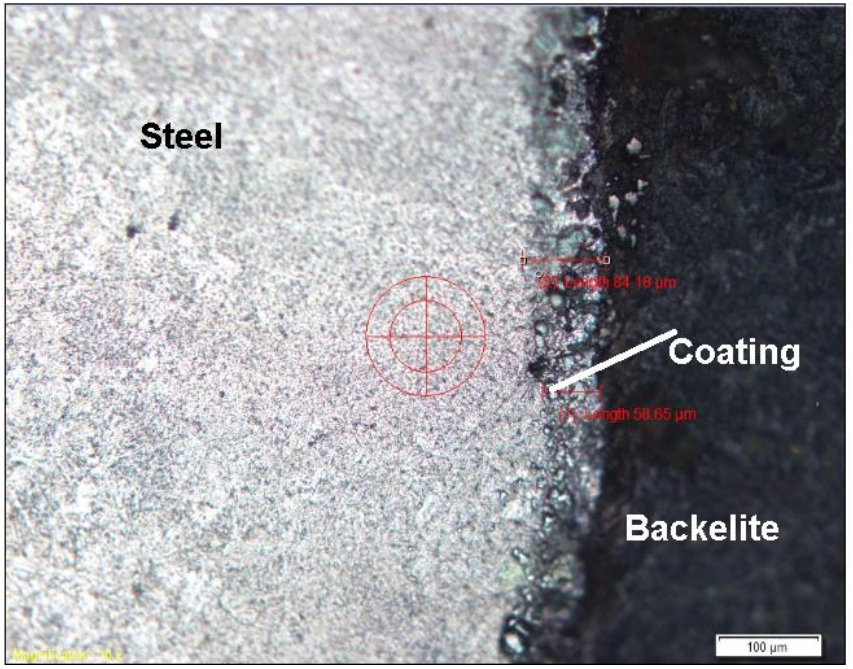


Thin layered red mud coating

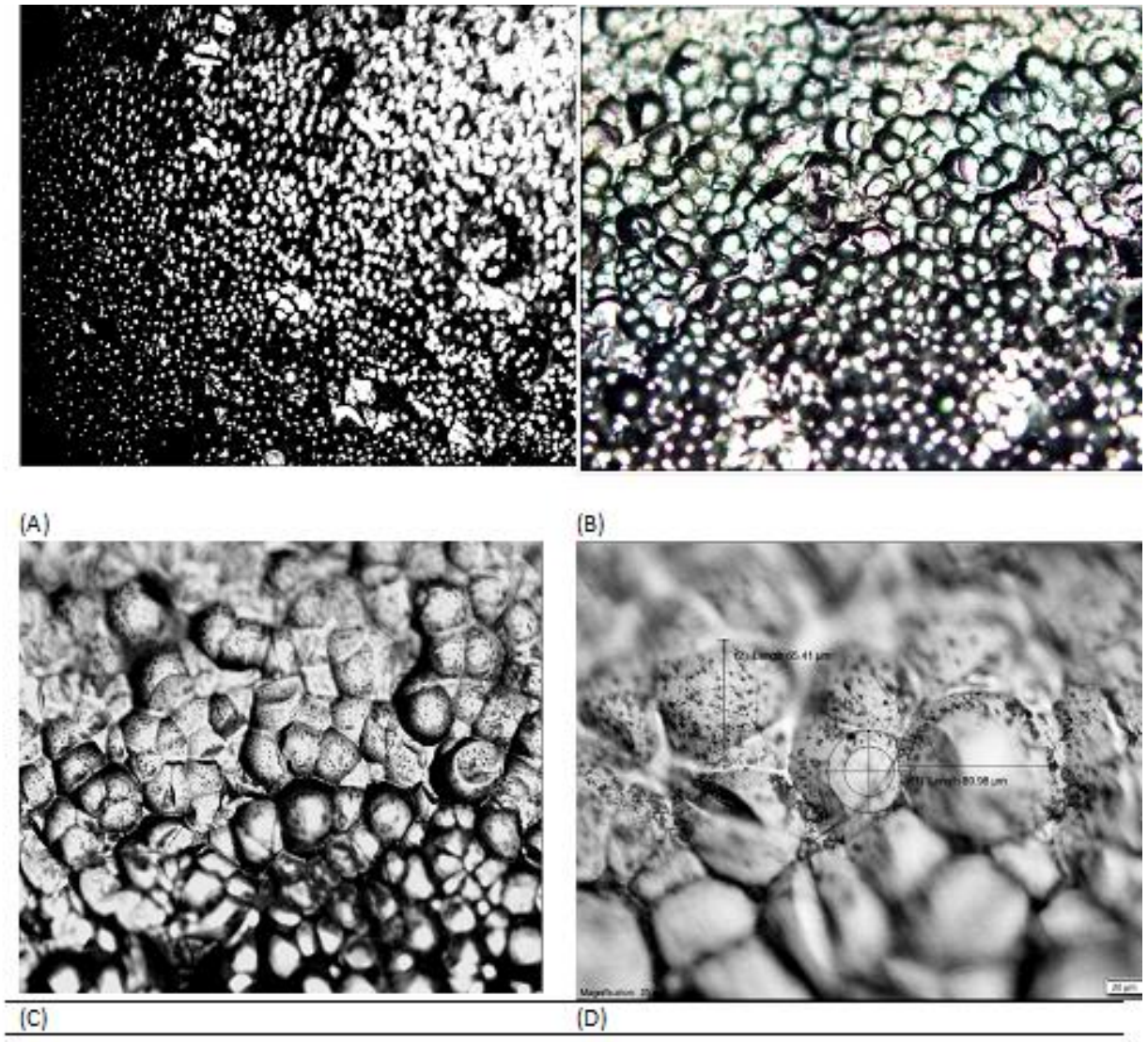
Thin layer coating X 50



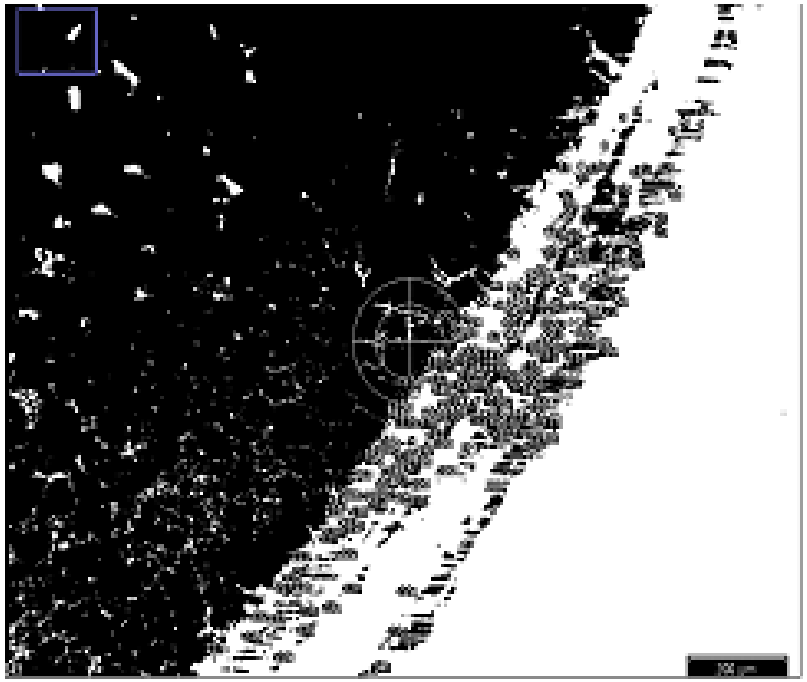
Thin layer coating X 100

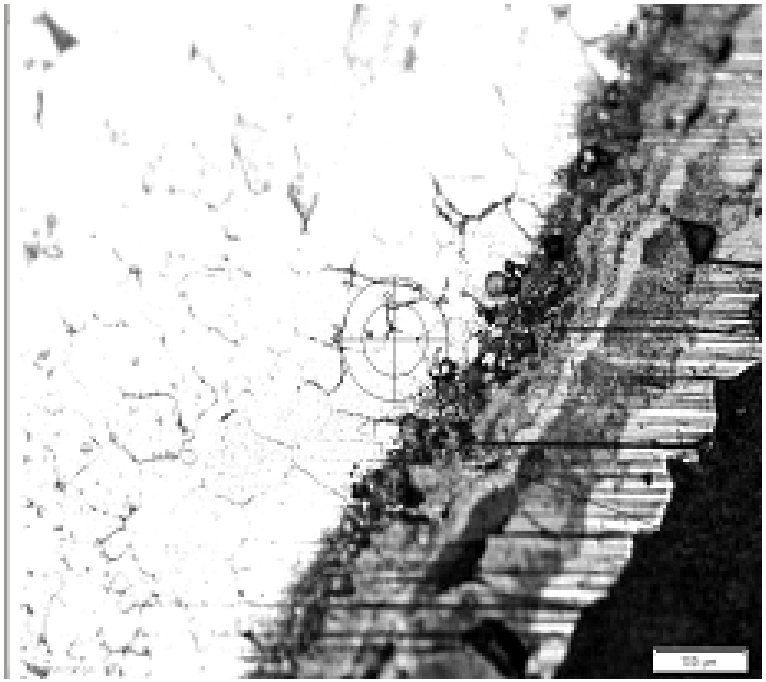


Surface of thin layered red mud coating (A X50, B X100, C X200, D X500)



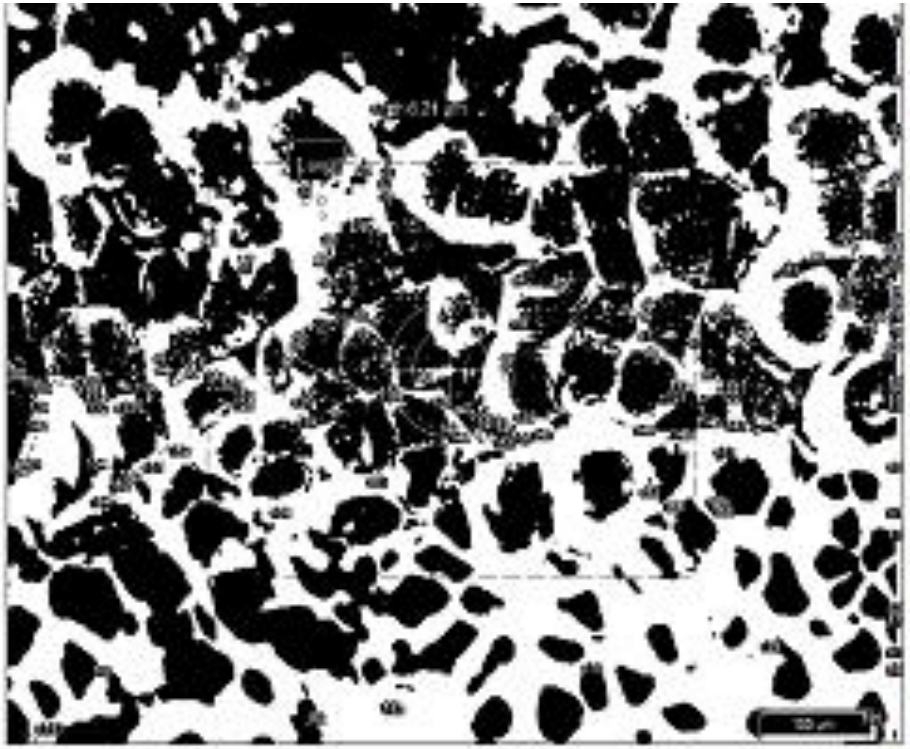
Analysis of porosity of red mud coating by using imageJ software

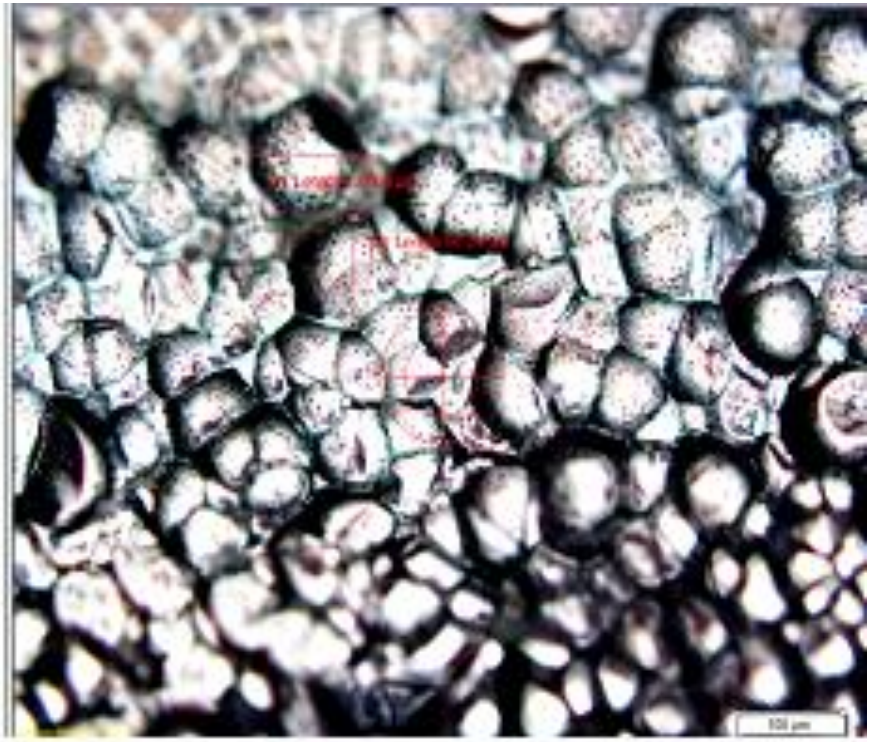




Slice	Count	Total Area	Average Size	%Area	Circ.	Solidity	Feret	FeretX	FeretY	FeretAngle	MinFeret
nocoranmx10.png	244	890.872	3.651	0.040	1	1	2.702	1008.278	722.646	135	1.911

Analysis of porosity of red mud coating by using imageJ software



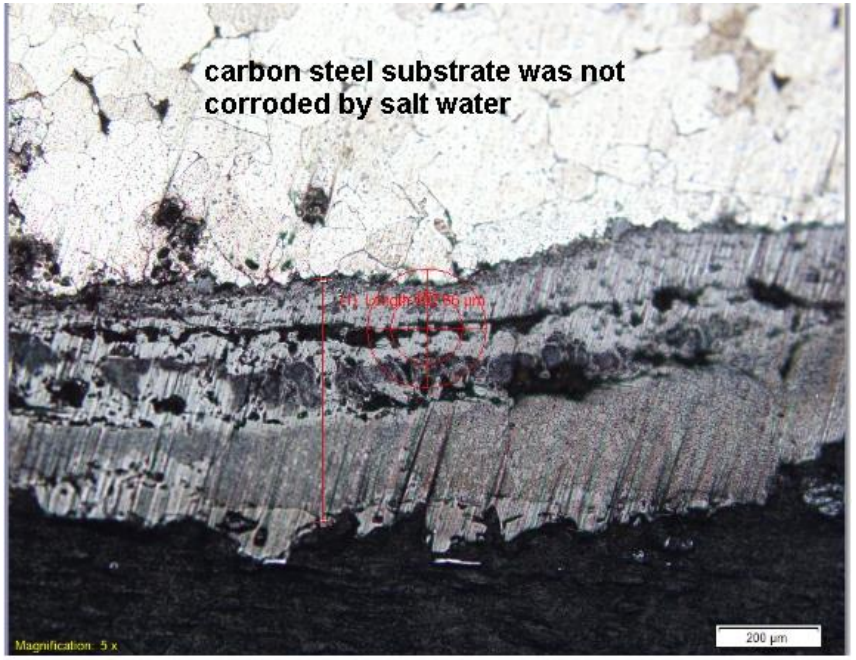


Slice	Count	Total Area	Average Size	%Area	Circ	Solidity	Feret	FeretX	FeretY	FeretAngle	MinFeret
surfacecoatingnanderiedX20.jpg	187	682.759	3.651	0.031	1	1	2.702	968.954	612.342	135	1.911

Microstructure after corrosion test

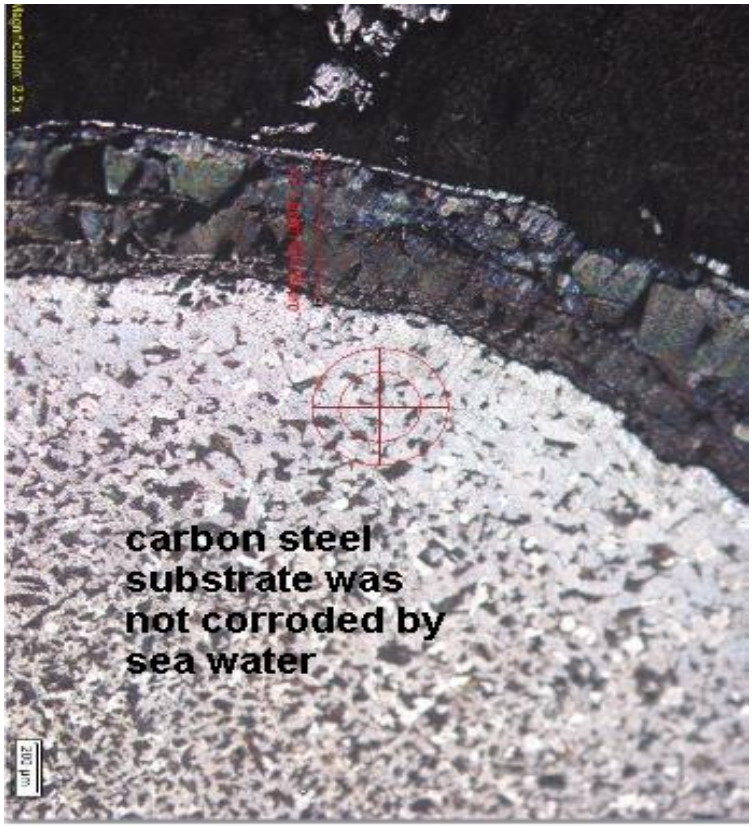
x50

X200



Microstucture after corrosion

x50



X100

Degradation of thin layered red mud coating by sea water

Conclusions

- In this research the characteristics of Saudi red mud was conducted to find the chemical compositions and crystal structures of this complex wastes to find its possible utilization.
- It was found that red mud is very coat able.
- The PH value was reduced to neutralize this waste .

Conclusions

- The ceramic coating from red mud was made and applied on low carbon steel substrate to improve surface hardness and corrosion resistance.
- The hardness of the coating was found 4.14 times higher than the metal substrate
- Diffusion of the atoms of red mud and substrate was observed from microstructures

Conclusions

- The red mud ceramic coating could be used on the external surface of waste water pipelines to save from erosion and corrosion.
- Red mud has environmental risk.
- Coordinated research should be carried out for processing and utilization of this waste.