

Manufacture of Modified Protective Coating Derived from Coal Industry

¹A.M.M. Saleh, ²A.A. El-Bassoussi, ³G.M. El-Kady and ³E.M. El-Naggar

¹Petroleum Applications Department,

²Department of Analysis and Evaluation,

Egyptian Petroleum Research Institute, Nasr City 11727, Cairo, Egypt

³Department of Applied Chemistry Faculty of Science, Azhar University, Egypt

Abstract: In this work, coal residue (pitch) was used to produce an inexpensive protective coating. The residue is primarily rehabilitated for just to be suitable for use as a coating material (reference coat) by dissolving it in benzene in a ratio of Pitch/Solvent(P/S) = 3:1 by weight. The reference coating was then mixed with polyurethane (commercial type) in percentages ranging from 5 to 15% by weight of the solid tar pitch. Well mature mortar cubes (7x7x7cm) with a (w/c = 0.4) and sand-cement (s/c = 2.75) were cast and covered with the prepared coatings. The cubes were then soaked individually in tap water, MgCl₂ 5% conc. and H₂SO₄ 3.0% conc. for different periods of time. The last two reagents represent sea water and 5 years complete immersion in sewage water respectively. The effect of reagents on the compressive strength, water retention and weight was measured for the cubes. The results revealed that, all prepared coatings gave satisfied physical characteristics. Addition of PUR up to 10% by weight of coal residue produced coating materials with the most favorable physical and chemical behavior.

Key words: Pitch • Coating • Sea water • Mortar

INTRODUCTION

Pitch represents from 30% to 60% of the coal tar. It is a very complex bituminous substance and has been estimated to contain about 5000 compounds. It is composed predominantly of the elements, carbon (about 93%) and hydrogen (about 4.5%) and small amounts of nitrogen, oxygen and sulfur compounds [1, 2]. Pitch is a thermoplastic material and possesses powerful adhesion to most surfaces, unique water resistance and moisture impermeability. Usually, pitch rehabilitation may be done by blending it with bitumen and rubber such as many vinyl-type polymers and copolymers. It is widely used in various branches of the economy among which electrical applications as electrode, roofing, damp proofing, waterproofing and coating for pipes [3-7]. Recently, coal tar pitch is used as a raw material for various mesophasic materials [8-10], a carbon / carbon composite matrix and carbon membranes [11-13]. Generally, carbon materials can be synthesized by pyrolyzing the organic precursor of tar pitch which are attractive candidates as anode materials for rechargeable lithium batteries [14]. On the other hand, a low softening point coal tar pitch is blended with a

molded and fired clay to be used in electrochemical applications [15]. Polymeric additives are also used to modify the rheological properties of pitch for application in building construction as insulating seal materials and anti-corrosion protective coating [8]. It is a known fact that, coal tar is a specific high boiling mixed solvent capable of dissolution of most polymers [16]. The most of polymers used are plastic waste types like PET, PAN, PS & ABS. The polymer is mixed in a ratio of 1:1 (w/w) at 800°C and then activated with a steam at 50% burn – off. This type of modified pitch show similar or better phenol adsorption properties than commercial activated carbons [17].

This paper describes a procedure for producing and evaluation of modified coal tar pitch with polyurethane suitable for use as a protective coating for mortar and concrete in different types of water (tap, sewage and sea).

MATERIALS AND METHODS

Experimental Work: The raw materials used in this study were as follows:

Corresponding Author: A.M.M. Saleh, Department of Petroleum Applications,
Egyptian Petroleum Research Institute, Nasr City 11727, Cairo, Egypt.
Tel: +202-22745902; Fax: 202-22747433; E-mail: aminaepri@yahoo.com.

- Waste tar pitch (T.P) obtained from El Nasr for Cock Industry and Basic Chemicals Co. (COKE) in Egypt
- Commercial polyurethane (PUR) under trade name of "Chemapore 312".
- Tap water, magnesium chloride ($MgCl_2$, 5% concentration) and Sulfuric acid (H_2SO_4 , 3.0% concentration). It must be mentioned here that, the last two reagents represent sea water and 5 years complete immersed in sewage water respectively [18]
- Benzene (Commercial grade)

Experimental Program: To achieve the research objective, the experimental program included four steps. The tests were achieved according to American Society for Testing and Materials (ASTM).

Characterization of Tar Pitch(T.P): Table(3-1) figure (3-1) illustrate the physical characteristics and Infrared Spectra (FTIR) using the instrument of model "Mattson – infinity series bench tab 961".

Primary Modification of the T.P: In this step, primary rehabilitation for tar pitch was done just to be suitable for use as a coating material (reference coat) by dissolving it in benzene in a ratio of Pitch/Solvent(P/S) = 3:1 by weight based on suitable characteristics for industrial application..

Modification of the T.P by Using Polyurethane (PUR): In this step, PUR was added in percentages ranging from 5 to 15% by weight of the solid tar pitch. The preparation of coating started after heating the calculated amount of pitch in a suitable container to a temperature ranging from 190-200°C and then mixed slowly for two hours with

Table (3.1): Characteristics of the Virgin Tar Pitch

Characteristic	ASTM Method	Result
Softening Point, °C	D36	70
Penetration @ 25 °C, 0.1 mm	D5	Zero
Ash Content, wt%	D146	0.16
Water Content, wt%	D2216	0.197
Density, @ 25 °C, Kg / m ³	D71	1000.314
Initial Curing Time, hrs	D1640	ND ^(*)
Final Curing Tim	D1640	1 Minute
Adhesion Degree	D3359	V. Good
Dry Layer Thickness, mm	D1005	1.8

*Not Determined for being solid

Table (3-2): Properties of Commercial Polyurethane

Properties	Results
Solid Content, wt%	98 – 100
Density @ 25 0 C, Kg / L	1.56±0.04
Viscosity @ 25 0 C, m.Pa.s	1500±500
Initial Curing Time @ 25 0 C, hrs	24
Final Curing Time, @ 25 0 C, Days	7

the desired volume of PUR. The previous determined amount of solvent was added in drop wise. The blend was stirred gently for another one hours to make sure of complete homogeneity before it was ready for use. The characteristics of the prepared coatings are illustrated in table (3.3).

Coating of Mortar Cubes

Mortar Cubes Preparation: Mortar cubes measuring (7× 7× 7 cm) using commercial grade of Ordinary Portland Cement (OPC) produced by " Helwan Company of Cement " with water-cement(w/c) and sand-cement (s/c) ratios of 0.485 and 2.75 respectively were prepared.

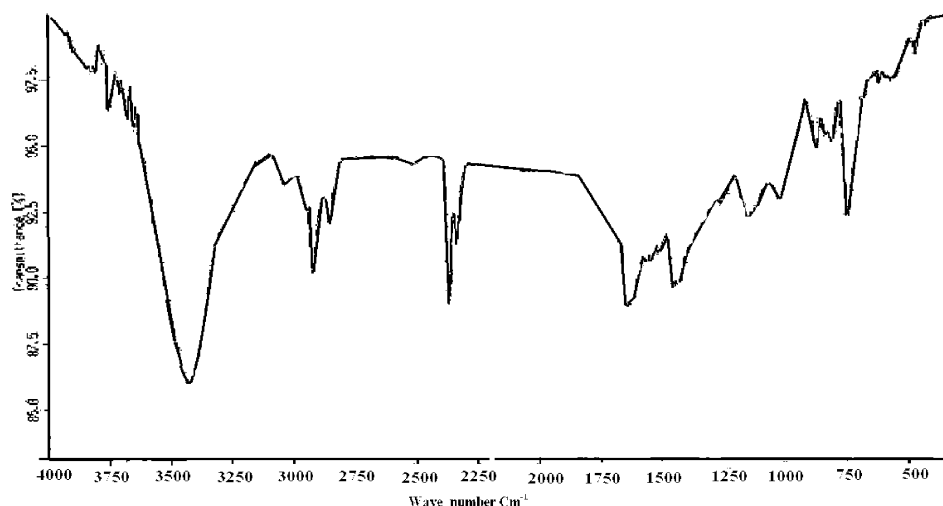


Fig. 3.1: FTIR Spectrum of waste tar pitch

Table (3-3): Characteristics of Modified Tar Residue

			Description			
			R.T.R	R.T.R ₅	R.T.R ₁₀	R.T.R ₁₅
Coating Application	Before	Solid Content, wt%	75	75	75	75
		Density @ 25 °C, Kg / L	1.092	1.101	1.112	1.122
		Saybolt Viscosity @ 30 °C, s	95	110	127	143
		Initial Curing Time, hrs	10	15	20	30
		Final Curing Time, Days	2	4	8	12
	After	Gloss	140	138	135	134
		Adhesion	V. Good	Excellent		
		Dry Layer Thickness, μm	180	180	180	150

The cubes were cast in standard moulds and water cured for a week and then left to dry and mature. Before coating application the surfaces of cubes were cleaned. The all prepared coatings were applied separately with a brush and then left to dry at room temperature.

Evaluation the Effect of All Prepared Coatings on the Performance of Mortar Cubes: In this step; water absorption (ASTM- C97), compressive strength (ASTM-C 109), chloride permeability (according to Ion Chromatography handbook) and chemical resistance (ASTM- 267) after complete immersion in different reagents for different periods of time (3,7,14,21&28 days) were determined knowing that;

R.T.R. = Primary modified tar pitch (reference sample).
 R.T.R.PU_{5,10&15} = Modified tar pitch containing Polyurethane in percentages of 5, 10 &15% by weight of the pitch respectively.

The rate of water retention and sorptivity values could be calculated using the following equations [19].

$$\text{Rate of water retention} = W_w / A_c t \text{ \& Sorptivity} = V_w / A_c t^{1/2}$$

Where:

W_w = Water weight gained by the specimens, (kg).

A_c = Cross sectional area of each specimen, (m^2).

t = Time of exposure, (hr)

V_w = Water volume absorbed by specimens, (m^3)

RESULTS AND DISCUSSION

Characteristics of Virgin Tar Pitch: It was detected from table(3-1) and figure (3-1) that, the absorbance at 3711 cm^{-1} is 1.41 as indicate that the coal tar contains high concentration of the alcoholic and phenolic components. It showed high absorption band at about 1920 cm^{-1} , which corresponds to C-H stretching in the aromatic components. The bands at about 1786 cm^{-1} indicated the presence of aldehydes, ketones, carboxylic

acids and some esters, mainly aromatic esters. Also, the percent of the polymeric compounds in the coal tar is found to be higher. At the band at about 1340 cm^{-1} indicating sulphones. The absorption band at about 2920 cm^{-1} and about 3030 cm^{-1} corresponding to the C-C stretching in alkanes.

Characteristics of Modified Coatings: The characteristics of prepared modified coatings are illustrated in table (3-3). The following results were obtained:

- Comparing to the reference sample, the characteristics of modified coatings showed noticeable increase in density and saybolt viscosity by the increase of the concentrations of polyurethane. The adhesion property was excellent on the addition of PUR. This may be attributed to the effect of PUR addition as well as the presence of the polar groups which increase the polar attraction of modified tar pitch to mortar.
- Initial and final curing times were also retarded (increased) while, the degree of gloss decreased as the amount of PUR increased. This may be explained by that, PUR is a material has low gloss characteristics and long final curing time.
- The dry layer thickness did not affected by the addition of PUR up to 10%. The two concentrations showed same thickness ($180 \mu\text{m}$). The addition of 15% PUR showed a decrease to $150 \mu\text{m}$. This may be attributed to increase in viscosity of the coating so, its workability was decreased.

Effect of the Different Chemical Reagents on Performance of Mortar Cubes

The Effect of Chemical Reagents on the Change in Weight of Mortar Cubes: The percent change in weight after complete immersion in all chemical reagents was illustrated in figures (3-2,3&4). It was detected that;

- Generally, there was a gradual increase in weight relative to immersion time in all reagents.

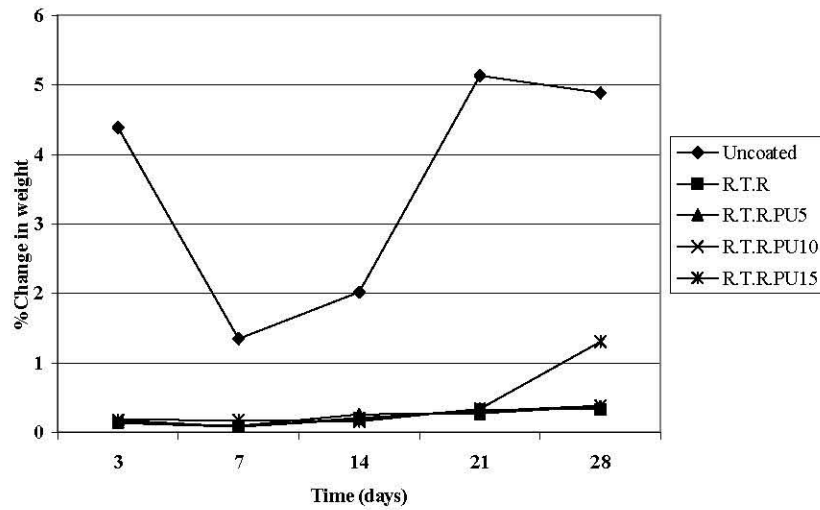


Fig. 3-2: % Change in Weight for Mortar Cubes Coated with Unmodified and Modified T.R after Immersion in Tap Water

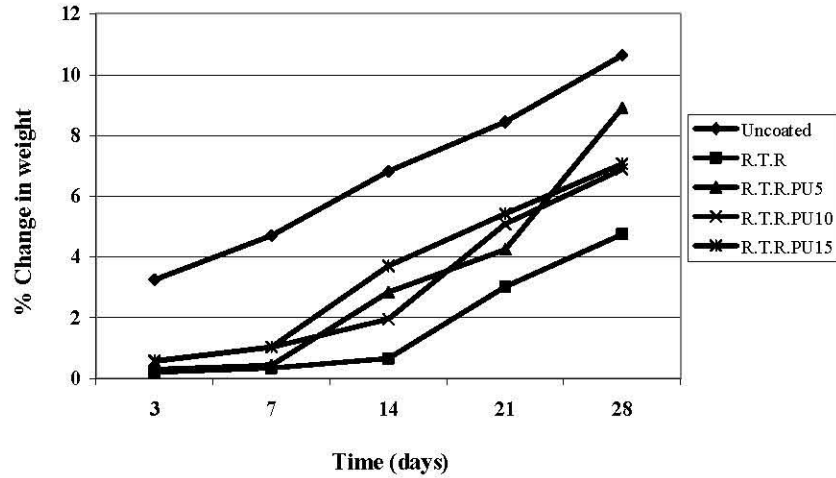


Fig. 3-3: % Change in the Weight for Mortar Cubes Coated with Unmodified and Modified T.R after Immersion in 3% Sulfuric Acid Solution

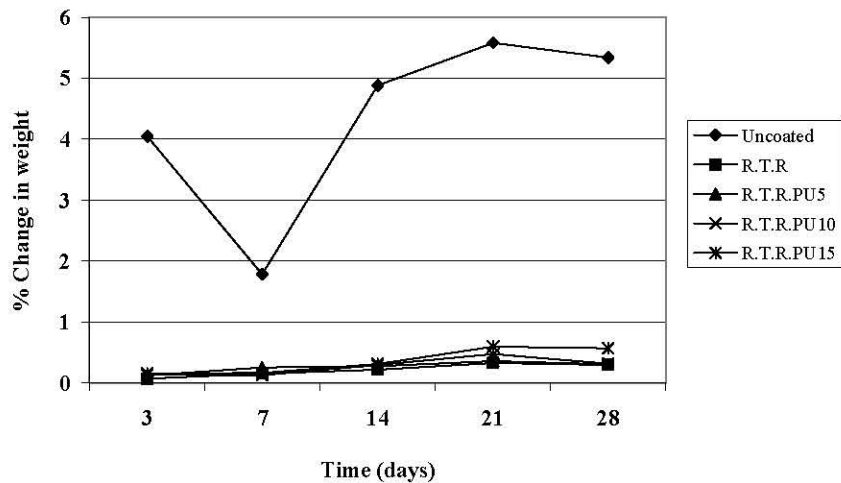


Fig. 3-4: % Change in Weight for Mortar Cubes Coated with Unmodified and Modified P.R after Immersion in 5% Magnesium Chloride Solution

Table (3-4): %Change in the weight for mortar cubes coated with unmodified and modified T.R after Immersion in 3% Sulfuric acid solution

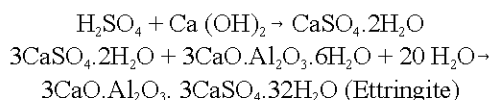
Immersion Time (day)	Change in Weight Percent Of Mortar Cubes				
	Uncoated	R.T.R	R.T.R.PU ₅	R.T.R.PU ₁₀	R.T.R.PU ₁₅
3	3.246	0.203	0.297	0.561	0.586
7	4.707	0.335	0.433	1.023	1.042
14	6.817	0.652	2.841	1.954	3.702
21	8.445	3.013	4.244	5.083	5.418
28	10.637	4.738	8.909	6.889	7.063

Table (3-5): Chloride Diffusion Resistance Using Ion Chromatography

Specimen	Chloride ion diffusion (ppm)
- Uncoated mortar cubes	548.6
- coated mortar cubes using:	
■ R.T.R 105	
■ R.T.R.PU ₅	107
■ R.T.R.PU ₁₀	112
■ R.T.R.PU ₁₅	114

In Case of Tap Water: This may be attributed to the motion of water molecules into the cubes, partial dissolution and leaching on immersion of mortar cubes in solutions.

In Case of Acid Solution: it may be as a result of reaction of H_2SO_4 acid and $Ca(OH)_2$. The final products were Calcium Sulfate " $CaSO_4$ " and water according to the following equation:



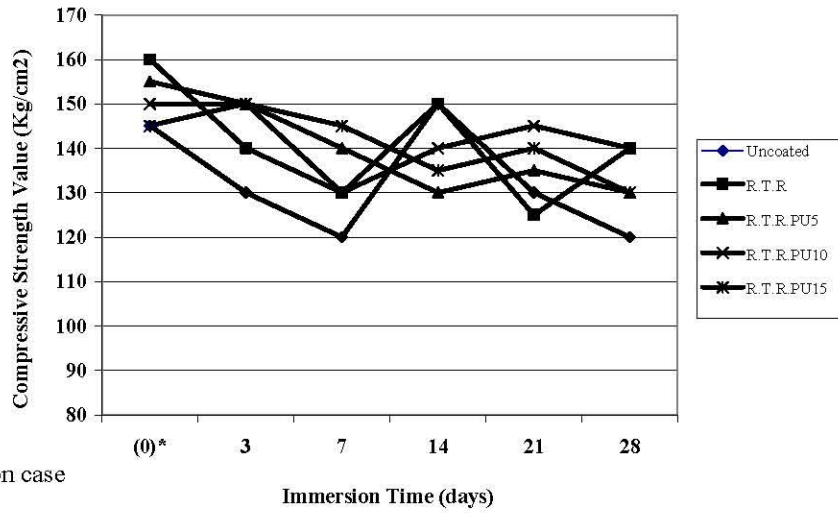
In Case of $MgCl_2$ Solution: This may be attributed to the formation and dissolution of a salt, blocking the pores, causing the apparent increase in weight.

- The uncoated cubes showed the highest weight percent increase which may be due to calcium hydroxide dissolution.
- All the coated mortar cubes showed a fluctuation in the percent change in weight. This phenomenon may be attributed to the random distribution of the water molecules on the surface of the mortar cubes. Furthermore, the interaction between sulfuric acid and polyurethane, would increased the porosity of the coating film and accordingly increases the leaching rate of calcium hydroxide.
- Generally, the values of percent change in the weight for the coated mortar cubes is always less than that recorded for uncoated mortar cubes. This may be attributed to water repellency of both tar residue and PUR, thus the water progress was hindered.

- For the uncoated mortar cubes, the calculated rate of water retention was lowered from $11.49 \times 10^{-3} \text{ Kg/m}^3/\text{hr}$ to $0.703 \times 10^{-3} \text{ Kg/m}^3/\text{hr}$ for coated cubes using R.T.R after immersion time of 28 days. For the coated mortar cubes, the calculated rate was increased as the percent of the polyurethane increased. This increase in the rate of water retention was $0.718 \times 10^{-3} \text{ Kg/m}^3/\text{hr}$, $0.788 \times 10^{-3} \text{ Kg/m}^3/\text{hr}$ and $1.313 \times 10^{-3} \text{ Kg/m}^3/\text{hr}$ on using R.T.R and R.T.R.PU_{5,10&15} respectively.
- The calculated values of sorptivity for both the uncoated and coated mortar cubes showed the same manner. It was 0.29 mm/hr for the uncoated mortar cubes and lowered to 0.0182 mm/hr, 0.0186 mm/hr, 0.0204 mm/hr and to 0.0340 mm/hr on using coated mortar cubes R.T.R and R.T.R.PU_{5,10&15} respectively.
- Table (3-5) illustrates the chloride diffusion resistance using ion chromatography technique. It was noticed that, the phenomenon of the chloride ion retention for different mortar cubes followed the same rout as that recorded by the water retention.

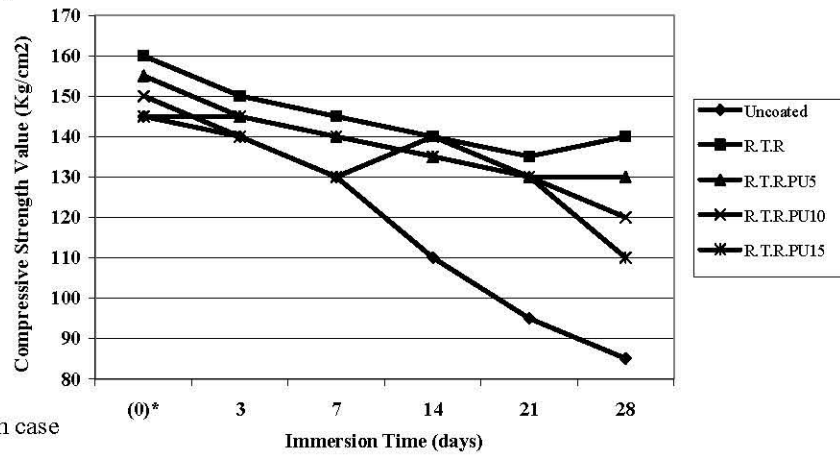
Effect of Chemical Reagents on the Compressive Strength of Mortar Cubes: Figures (3-5,6&7), show the effect of different reagents on the compressive strength value of immersed all mortar cubes for different intervals of time. Generally, it was noticed that;

- For cubes uncoated and coated with R.T.R, The value of compressive strength increased from 145 to 160 Kg/cm^2 . This may be attributed to the use of pitch which acts as a strengthen material and closes, to some extent, the pores of the external surface mortar cubes.
- In case of using the coal tar modified with PUR, the value of the compressive strength decreased as the concentration of polyurethane increased. The compressive strength value decreased from 160 Kg/cm^2 to 155 Kg/cm^2 , 150 Kg/cm^2 and 145 Kg/cm^2 on using mortar cubes coated with R.T.R and R.T.R.PU_{5,10&15} respectively. This may be attributed to the increase of viscosity the mixture.



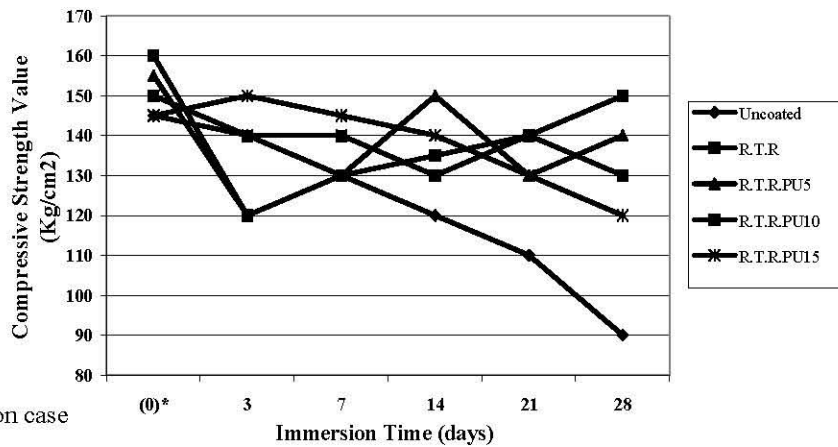
(o)*: Before Immersion case

Fig. 3-5: Effect of Tap Water on the Compressive Strength Values of Mortar Cubes Coated with Unmodified and Modified T.R



(o)*: Before Immersion case

Fig. 3-6: Effect of 3% Sulfuric Acid Solution on the Compressive Strength of Mortar Cubes Coated with Unmodified and Modified T.R



(o)*: Before Immersion case

Fig. 3-7: Effect of 5% Magnesium Chloride Solution on the Compressive Strength of Mortar Cubes Coated with Unmodified and Modified T.R

In Case of Tap Water: For the uncoated mortar cubes the obtained values of the compressive strength followed the same manner as that recorded the percent change in weight before and after immersion. This may be attributed to the motion of water molecules into the mortar cubes itself.

In Case of Acid Solution: For the uncoated mortar cubes, the compressive strength values decreased from 145 Kg/cm² to 85 Kg/cm² after immersion time of four weeks (28 day). The percent change is 41.4%, with an estimated rate of decrees was 2.14 Kg/cm²/day. This may be attributed to the reaction of sulfuric acid with calcium hydroxide producing gypsum, which in turn reacts with calcium aluminates in the cement material of the cubes to produce Ettringite, which has low compressive strength, as mentioned before.

In Case of Mgcl₂ Solution: For the uncoated mortar cubes, the value decreased from 145 Kg/cm² before immersion to 90 Kg/cm² after immersion for a period of four weeks with an estimated rate of 1.964 Kg/cm²/day.

- For coated specimens in tap water, the obtained values of compressive strength followed the same route as weight change after immersion for four weeks. This may be attributed to the motion of water molecules into the mortar cube itself as mentioned before. The rates of change in the compressive strength for the coated mortar cubes were lower than that of the uncoated mortar cubes. For example, after 28 days immersion time, the compressive strength value was lowered from 145 Kg/cm² to 120 Kg/cm² with percent of 17.2% on using the uncoated mortar cubes, while it lowered from 160 Kg/cm² to 140 Kg/cm² and from 150 Kg/cm² to 140 Kg/cm² in the percentage of 12.5% and 6.6% in the case of using R.T.R and R.T.R.PU₁₀ respectively. This may be attributed to T.P and PUR characteristics.
- For coated specimens in acid solution, The estimated rate of compressive strength decreased from 2.14 Kg/cm²/ day to 0.714 Kg/cm² /day for uncoated and coated mortar cubes with using R.T.R respectively. This may be attributed to the characteristics of the coal tar as a water repellant material that may decrease the effect of sulfuric acid on the mortar cubes. On the other hand, the estimated rate was increased to 0.89 Kg/cm²/day, 1.07 Kg/cm²/day and 1.25 Kg/cm²/day in the case of using R.T.R.PU_{5,10&15} respectively. This may be attributed to increase the rate of the action of sulfuric acid as mentioned before.

- For coated specimens in MgCl₂, the compressive strength values were decreased at the end of immersion time (28 days) in spite of the values changed up and down for the other immersion times (7, 14& 21 days). It may be attributed to the effect of MgCl₂ on the mortar constituents and to the motion of water molecules from one layer to another, so surface and internal pores in the cubes opened and closed based on this motion. For coated mortar cubes with (R.T.R) it was noticed that, the values of compressive strength was decreased from 160 Kg / cm² before immersion to 120 Kg / cm² after 3 days of immersion. Then, it increased by time to 130 Kg / cm², 135 Kg / cm², 140 Kg / cm² & 150 Kg / cm² for 3, 7, 14, 21, 28 days immersion time. This may be explained by that the effect of MgCl₂ on mortar constituents was very rapid at first few days of immersion (first case). On the other hand, the compressive strength values increased by time because of the formed salts closed to some extent the pores present in the cubes. For coated cubes with R.T.P.PU₅ and R.T.P.PU₁₀ also, the compressive strength values decreased from 155 Kg / cm² to 120 Kg / cm² and from 150 Kg / cm² to 140 Kg / cm² respectively after 3 days of immersion. This may be a result of water motion.

CONCLUSION

In this research, waste tar pitch was modified to produce a local coating materials have special characteristics to be suitable for use in both sewage water and sea water medias using PUR, the most popular material used on commercial scale, up to 15% by weight of the residue. The prepared coating materials were used to coat mortar cubes which are totally immersed for four weeks -representing sever condition- in different chosen chemical regents as tap water, H₂SO₄(3% conc.) and MgCl₂(5% conc.). The last two chemicals representing both sewage water and sea water respectively. Both change in weight and compressive strength values were measured for the uncoated and coated mortar cubes before and after immersion. The net results show that:

- All prepared coatings gave satisfied physical characteristics.
- Addition of PUR up to 10% by weight of coal residue produced coating materials with the most favorable physical and chemical behavior.
- Modification of tar pitch with PUR in the percentage of 15% may be not recommended specially in acidic media.

REFERENCES

1. Kuriakose, A.P. and S.K.B. Manjooran, 1994. Utilization of refining sludge for lighter oils and industrial bitumen, *J. Energy& Fuels*, ACS Publications, 8(3): 788-792.
2. Sheu, E.Y., M.M. De Tar and D.A. Storm, 1991. Rheological properties of vacuum residue fractions in organic solvents, *J. Fuel*, Elsevier, 70(10): 1151-1156.
3. Mehta, P.K. and B.C. Grewick, 1996. In Proceeding of International Conference on Concrete in the Service of Mankind, University of Dundee, Scotland.
4. Maslehuddin, M., H. Saricimen and M. Al-Mana, 1987. Effect of fly ash addition on the corrosion resisting characteristics of concrete, *J. ACI Materials*, American Concrete Institute, January- February, 42-50.
5. Rasheeduzzafar, R., F.H. Dakhil and A.S. Al-Gahtany, 1984. Deterioration of concrete structures in the environmental of the Middle East, *J. ACI Materials*, American Concrete Institute, 81(1): 13-20.
6. Mehta, P.K., 1991. Durability of concrete – fifty years of progress?, 1991, Second International Conference on Durability Of Concrete. August 4-9, Monteral, Canada, I: 1-31.
7. Bardon, C., L. Barre, D. Espinat, V. Guille, M.H. Li, J. Lambard, C. Ravey, E. Rosenberg and T. Zemb, 1996. The colloidal structure of crude oils and suspensions of asphaltenes and resins, *J. Petroleum Science & Technology*, Marcel Dekker, New York, Y.N, 14(1-2): 203-242.
8. Brzozowska, T., J. Zielin and J. Machnikowski, 1998. Effect of polymeric additives to coal tar pitch on carbonization behavior and optical texture of resultant cokes, *J. Analytical and Appl. Pyrolysis*, Elsevier, 48(1): 45-58.
9. Legin-Kolar, M., M.A. Radenovic' and D.Ugarkovic', 1999. Changes in structural parameters of different cokes during heat treatment to 2400°C, *J. Fuel*, Elsevier, 78(13): 1599-1605.
10. Vulava, M.V., L.D. McKay, G.S. Driese, F. Menn and S. Saylor, 2007. Distribution and transport of coal tar-derived PAHs in fine-grained residuum, *J. Chemosphere*, Elsevier, 68(3): 554-563.
11. Honda, H., 1988, Carbonaceous mesophase: history and prospects, *J. Carbon*, Elsevier, 26(2): 139-156.
12. Mochida, I., S.H. Yoon, Y. Korai, K. Kammo, Y. Sakai and M. Komatsu, 1993. Mesophase pitch- Synthesis and its applications, *CHEM-TECH*, 04.
13. Liang, C., G. Sha and S. Guo, 1999. Carbon membrane for gas separation derived from coal tar Pitch, *J. Carbon*, Elsevier, 37(9): 1391-1397.
14. Sik Kim, J., 2001. Charge/ discharge characteristics of the coal tar pitch carbon as negative electrode in Li-ion batteries, *J. power sources*, Elsevier, 97-98: 70-72.
15. Montillaa, F., E. Morallo'na, J. Va'zqueza, L. Alcan'iz-Mongeb, J. Cazorla-Amoro'sb and. A. Linares-Solanob, 2002. Carbon-ceramic composites from coal tar pitch and clays: application as electro catalyst support, *J. Carbon*, Elsevier, 40(12): 2193-2200.
16. Machnikowski, J., H. Machnikowska, T. Brzozowska and J. Zielin' ski, 2002. Mesophase development in coal-tar pitch modified with various polymers, *J. Analytical and Appl. Pyrolysis*, Elsevier, 65(2): 147-160.
17. Diez, M.A., C. Barriocanal, Lorenc-Grabowska, G. Gryglewicz, and J. Machnikowski, 2009. Suitability of plastic wastes and coal – tar pitch as precursor of carbon.", 1st Spanish National Conference on Advances in Materials Recycling and Eco – Energy, Madrid.
18. Render, J.A., E.J. Esfandi and R.P. Hsi, 1991. Evaluation of protective coatings for concrete exposed to sulfide generation in waste water treatment facilities, *Journal of Protective Coating & Lining*, Society for Protective Coatings, 8(11): 48- 56.
19. Almusallam, A.A., F.M. Kan, S.U. Dulaijan and O.S.B. Al-Amoudi, 2003. Effectiveness of surface coatings in improving concrete durability, *J Cement & Concrete Composites*, Elsevier, 25(4-5): 473-48.