Technical Paper

ISSN 1997-1400 Int. J. Pavement Res. Technol. 8(6):426-432

Mix Design and Moisture Susceptibility of Asphalt Concrete Mixes Containing Waste Catalyst from Oil Refineries

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Abstract: The main objective of this study was to investigate the potential of using spent catalysts produced from the process of refining crude oil as a constituent material in hot mix asphalt (HMA). Two types of spent catalyst; equilibrium catalyst (ECat) and zeolite catalyst (ZCat) were used to partially replace some selected sizes of aggregate in the HMA. Chemical analysis of the raw catalysts indicated that both catalyst types used in this study comprised mainly of Al_2O_3 and SiO_2. Marshall Method of mix design was followed to determine the optimum asphalt content of the aggregate structure containing waste catalyst. Volumetric and stability data indicated that there is a good potential for using spent catalyst in road applications. Environmental analysis and moisture damage potential were also carried out to further characterize the designed mixes. It was observed that the level of all toxic elements in both ECat and ZCat spent catalysts samples were within the acceptable limits. ECat mixes proved to be less susceptible to moisture damage compared to the ZCat mixes. For the amounts of catalyst used in this study, the ZCat mixes failed to meet the moisture resistance requirements of 80% retained strength and hence it is not recommended to be utilized as a filler material.

DOI: 10.6135/ijprt.org.tw/2015.8(6).426
Key words: *Asphalt mixes; Moisture susceptibility; Waste catalyst in roads; Waste recycling.*

Introduction

Hot mix asphalt (HMA) is the most common material used for paving applications. It primarily consists of asphalt cement and mineral aggregates. The asphalt cement acts as an adhesive agent that binds aggregate particles into a cohesive mass. When bound by asphalt cement, mineral aggregate acts as a stone framework that provides strength and toughness to the system. The behavior of HMA depends on the properties of the individual components and how they react with each other in the system. In addition to the HMA's conventional components of asphalt cement and aggregates, attempts are constantly made to incorporate some unconventional materials into HMA in order to enhance its performance or as part of the efforts to build more sustainable, environmentally-friendly road structures. An example of such materials is waste catalysts produced during the refining process of crude oil.

A catalyst is a chemical agent that accelerates chemical reactions. What differentiates it from other chemical substances is that whilst it is involved in the reaction, it is not consumed by it. Catalysts are widely used in many industrial processes, especially petroleum refineries, but are wasted at the end as by-products. These wasted catalysts are also known as spent catalysts. Spent fluid catalytic cracking (FCC) catalyst, produced from the cracking of petroleum in the oil-refinery industry, is a waste material consisting mainly of active silica and alumina [1].

Different studies were conducted on the nature of the spent catalyst and its toxicity. Some considered the spent catalyst to be hazardous and others considered it as non-hazardous which could be due to the difference in the process used inside refineries. Furimsky [2] states that among spent solid refinery catalysts, hydroprocessing catalysts, especially those from upgrading of heavy feeds, are much more contaminated than the FCC and reforming catalysts because the feed stocks processed in the FCC and reforming operations are either of a conventional origin or were already catalytically treated. In the USA and Canada, among solid refinery catalysts, only spent hydroprocessing catalysts are being classified as hazardous wastes, although this may not be the case in other parts of the world [3]. This classification is based on the leachability, flammability and toxicity of the catalysts. The spent (equilibrium) fluid catalytic cracking (FCC) catalysts are not classified as hazardous wastes. They are non-flammable and their leachability is in compliance with the USA Environmental Protection Agency (EPA) regulatory levels. According to the results of Su et al. [4], such catalyst should be classified as non-hazardous, and instead of being disposed the material could very well be utilized in the cement and concrete industries since no leaching of heavy metals was detected.

The fact that some types of catalysts were considered non-hazardous motivated some researchers to investigate the possibility of using those catalysts as a construction material. In a study done by Su et al. [5] to examine the feasibility of reusing spent zeolite catalyst, which mainly contains SiO_2, Al_2O_3 and CaO (material was provided by China Petroleum Company, Taiwan), as a substitute for fine aggregate in cement mortars, the results show that spent catalyst can replace up to 10% of the fine aggregate (sand) without decreasing the mortar's strength. In another study done by Rattanasak [6] on the possibility of using spent catalyst (provided by Thai Oil Company) as a concrete constituent, the material was evaluated as a sand replacement and as a partial replacement of cement after grounding. Results indicated that the compressive strength of mortars containing spent catalyst at the proportion of 1.25 times of cement, by weight was strong enough to make a

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Note: Submitted January 21, 2015; Revised October 6, 2015; Accepted October 11, 2015.

concrete brick. Paya et al. [7] carried out a specific feasibility study of reusing spent catalyst in cement mortars in which fluid catalytic cracking catalyst residue (FC3R) was verified as a good pozzolanic material. The results indicated that the catalyst can substitute up to 20% of cement without affecting the mortar's quality. It is worth noting that most of the studies conducted on the reuse of spent catalyst focussed on incorporating spent catalyst in concrete due to the similarity of the chemical and physical properties of spent catalyst to Portland cement and sand. The large contents of SiO_2 and Al_2O_3 in the spent catalyst participate in the process of cement hydration [8, 9].

Despite the efforts made by the concrete industry to utilize spent catalyst in its products, asphalt industry however, does not seem to share similar interest. Literature search on the use of spent catalyst in asphalt products is almost none existing. Furimsky [2] recommends the use of FCC catalyst as filler material. The recommendation includes reducing coarse spent catalyst to the required filler size and incorporating it in the asphalt mix in the range of 3% to 5% by weight of aggregate.

Objective and Scope

As mentioned earlier, there are huge volumes of two types of waste catalysts produced in oil refineries in Oman. These are equilibrium catalyst (ECat) from Mina Al-Fahl refinery and zeolite catalyst (ZCat) from Sohar refinery. All the spent catalyst quantities are dumped and there are no real efforts of any reclamation. The main objective of this study was investigating the potential use of spent catalyst produced from local refineries as a constituent material in asphalt mixes. The ultimate goal was to beneficially utilize spent catalyst in order to minimize the environmental and economic burden associated with storing it in landfills. The use of spent catalyst as a constituent material in asphalt mixes was envisaged to take one of two forms: either as aggregate replacement or as a filler material. Relatively coarse spent catalyst particles (greater than 0.075 mm) were used to replace some corresponding sizes of aggregate particles to act as part of the aggregate skeleton. Finer spent catalyst materials were incorporated as a filler to form an asphalt cement extender in the mix. Moisture susceptibility and environmental analysis were also carried out to further characterize the designed mixes.

Production and Storage of Spent Catalysts

The quantity of spent catalyst produced from different processing units depends to a great extent on the amount of fresh catalysts used, their life and the deposits formed on them during their use in the reactors. Approximately 20-25 tons per day of ZCat spent catalyst are generated at the Sohar Refinery and the material produced has essentially a fine powder form. The spent catalyst is collected in a1000 kg bags and all existing material (close to 20,000 tons) are stockpiled on the refinery premises itself along with other two dumping sites. The ECat spent catalyst from Mina Al-Fahl refinery is collected in one ton (1000kg) bags and stored in shaded yards.

Material Characterization

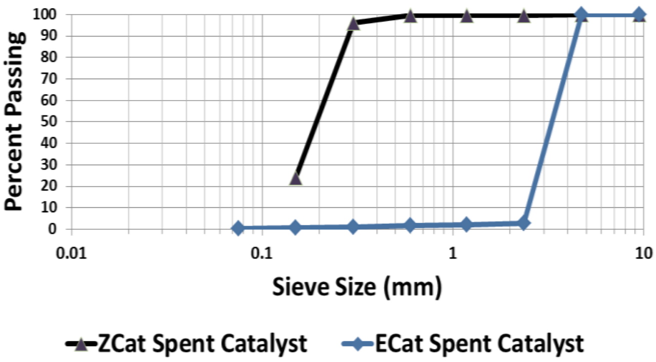

Fig. 1. Particle Size Distribution for ECat and ZCat Catalysts.

Spent Catalyst

Since this is the first attempt to incorporate spent catalyst in road applications, it was imperative to characterize the material in its raw form in order to determine its key physical and chemical properties. Several containers of the Ecat catalyst were collected. The material samples were collected from random locations at the disposal site. Furthermore, containers of the ZCat catalyst were shipped to the laboratory. Visual inspection of the raw materials showed that the physical state of both spent catalysts is solid. ECat spent catalyst has white to off-white colour. It is granular in shape and appears to be composed largely from 4 mm diameter spherical beige grains with an acidic smell. ZCat spent catalyst is grey in colour. It is odourless crystalline powder.

Gradation

Sieve analysis was performed on spent catalyst material from both sources in accordance with AASHTO T88. Fig. 1 shows the particle size distribution of both types. Results of the sieve analysis indicated that the ZCat is finer in nature than ECat.

Other Physical Properties

The bulk specific gravity test was conducted according to ASTM D854 to compare the results with established values for conventional aggregates. Results are presented in Table 1 along with other physical properties. The average specific gravity was 2.800 for the ECat and 2.600 for the ZCat. These two values are within the range of the specific gravity for sands.

The toughness of spent catalyst from the ECat was obtained from the Los Angeles abrasion test (ASTM C131). The average Los Angeles abrasion value was 72.4% as presented in Table 1. This high percentage of loss in weight indicates the soft nature of the material and it exceeds the 25%-35% limit established for aggregates used in asphaltic pavements according to the Oman standard specifications for road and bridge construction. The Los Angeles abrasion test was not conducted on the ZCat since it is in a powder form.

The sand equivalent value according to ASTM D2419 for the ECat was found to be 92.6% on average.

Chemical Analysis

Table 1. Physical Properties of Spent Catalysts.

Parameter	ECat	ZCat
Liquid Limit, %	51.9	72.8
Bulk Specific Gravity	2.800	2.600
Sand Equivalent, %	92.6	-*
Los Angeles Abrasion, %	72.4	-*

* These tests are not performed on fine materials

Table 2. Chemical Constituents of the ECat and ZCat Catalysts.

Chemical Constituents	Constituent (%) in ECat Spent Catalyst	Constituent (%) in ZCat Spent Catalyst
SiO_2	1.7	39.21
Al_2O_3	66.7	37.68
Fe_2O_3	0.07	0.66
CaO	0.08	0.05
MgO	0.02	0.26
Na_2O	8.29	0.43
K_2O	0.26	0.06
%LOI	26.13	2.43
Moisture	10.16	0.74

Table 3. Mass of Trace Elements in the ECat and ZCat Catalysts.

Trace Element	Mass in ECat (mg/kg)	Mass in ZCat (mg/kg)
Manganese (Mn)	111.8	20.25
Copper (Cu)	52.02	9.42
Zinc (Zn)	11.06	4.19
Stronium (Sr)	131.7	10.03
Iron (Fe)	892	161.62

Samples from both spent catalysts; ECat and Zcat were analyzed to determine the amounts of oxides, heavy metals, and volatile content (organics). Powdered solids of spent catalyst were acid digested for oxides and heavy metals analysis by Atomic Absorption Spectrometry (AAS) according to Method 3050B. Oxides analyzed by this method are Al_2O_3, Fe_2O_3, Na_2O, K_2O, CaO, MgO, and SiO_2, while the metals analyzed are Mn, Cu, Zn, Sr, and Fe. Tables 2 and 3 provide a summary of the obtained results (oxides and heavy metals) for both spent catalysts. The ECat contained mainly Al_2O_3 (66.7%). The other oxides (Fe_2O_3, Na_2O, K_2O, CaO, MgO) were relatively low in concentration. Furthermore, about 26% of Ecat was found to be volatile organics (reported as lost in ignition, LOI). On the other hand, the total amount of trace (heavy) metals was about 1.2 parts per thousand (ppt). Iron was found to form the highest percentage (74%) of the total amount of heavy metals in the Ecat while zinc is the lowest (1%). The as received moisture content was around 10%.

The Zcat comprised mainly of approximately equal amounts of Al_2O_3 (37.7%) and SiO_2 (39.20%). The amount of CaO was relatively high (10%) compared to ECat (2.4%). The amounts of the tested oxides (Fe_2O_3, Na_2O, K_2O, MgO) were in the range of about 0.06% to 0.66%. Moreover, the amount of volatile organics (LOI) was found to be around 2.43% indicating much lower organic compounds content compared to the ECat. On the other hand, the total amount of trace (heavy) metals in Zcat was about 0.2 parts per thousand (ppt) (compared to about 1.2 ppt for ECat). Iron was found to form the highest percentage (79%) of the total amount of heavy metals while zinc is the lowest (2%). The as received moisture content was about 1%.

Aggregates and Asphalt Cement

Aggregate was obtained from a local asphalt plant. Four different aggregate stockpiles were used to design the aggregate structure of the base asphalt mix. These were 20 mm and 10 mm coarse aggregate sizes and 0-5 mm sand. In addition, mineral filler was also used. The aggregates were fractioned into individual sizes and recombined to produce a specific gradation. Oman specifications for HMA require that the particle sizes of the blended aggregate be within a certain gradation band. Three classes of wearing course gradations (A, B, and C) depending on the maximum aggregate size are recommended by the specifications. Class A represents the coarsest gradation with a nominal maximum aggregate size (NMAS) of 19.0 mm while Class C is the finest blend with a NMAS of 9.5 mm. No specific guidelines are given in the specifications on the particular uses of each class. The target blend gradation was formulated to meet the requirements of class B gradation as the most commonly used blend in local practice. The details of the aggregate blending are shown in Table 4 together with the specifications limits. The asphalt cement used was a straight run penetration grade 60/70.

Mix Design

The main objective of this task was to incorporate spent catalyst in asphalt mix by replacing specific fractions of aggregate in the control mix with spent catalysts from both sources. As mentioned earlier, the control mix is a wearing course class B mix according to Oman specifications for roads and bridge construction. Examining the particle size distribution of the raw spent catalyst and aggregate blend showed that the ECat is coarse enough to act as aggregate replacement in the size range of 4.75 mm to 2.36 mm of the target aggregate blend. This replacement resulted in using a significant amount of about 20% of the catalyst by weight of aggregate. On the other hand, the Zcat was more like mineral dust and hence it was decided to use it as mineral filler in HMA. The filler material in the target aggregate blend was fully replaced by the Zcat catalyst resulting in 5.5% by weight of aggregate being used. It is worth noting that those amounts of catalyst are relatively high and were likely not to result in acceptable mixes but the idea was to initially try to use the maximum practical amount of spent catalyst (as permitted by the aggregate gradation used) as the starting point for incorporating the catalyst in asphalt mixes

The Marshall Mix design method (AASHTO T245) for heavy traffic category was followed. For each aggregate structure used, several asphalt cement contents at increments of 0.5% were used during the mix design process.

Three specimens were compacted at each trial asphalt cement content using the Marshall compactor. The bulk specific gravity of the compacted specimens was then measured according to AASHTO T 166 standard test procedure. For the maximum theoretical density determination, a set of two identical specimens in the loose condition of the same mix was used and the measurement was carried out according to AASHTO T 209 standard. The air void

Table 4. Aggregate Blending and Target Blend Gradation.

Sieve size, mm	Stockpiles				LL specs	UL specs	Target Blend
	No. 20	N0. 10	Sand	Filler			
19.0	100	100	100	100	100	100	100
12.5	75	97	100	100	90	100	95
9.5	23	93	100	100	73	93	86
4.75	10	48	98	100	51	71	64
2.36	4	19	79	100	34	54	44
1.18	3	8	52	100	22	38	29
0.60	2	4	41	100	18	30	23
0.30	0	3	25	99	10	22	16
0.15	0	3	18	98	9	17	13
0.075	0	0	4	51	2	8	4
% Agg. in the Blend	15.0	41.5	38.0	5.5			

was then calculated. Full volumetric analysis was then carried out to determine the rest of volumetric and physical properties at each trial asphalt cement content. Finally, the Marshall test was carried out on the compacted specimens to determine the stability and flow values. The Marshall stability and flow values along with density, air voids in the total mix, voids in the mineral aggregate, and voids filled with asphalt were used for determining the optimum asphalt content that satisfies certain specification requirements.

The optimum asphalt cement content is generally selected as the asphalt content satisfying the air void specification limits. The air void limits in the Omani specifications for wearing course are set to be in the range 4.0– 7.0 %. Therefore, the optimum asphalt cement content is selected at the content that corresponds to an air void level within that range. Other properties were then checked at that asphalt cement content and then compared with the specification requirements. The results of the mix design of asphalt mixes made with ECat spent catalyst are presented in Table 5 together with the specification requirements.

Despite the fact that the stability values obtained for the designed mix are reasonably high at all asphalt cement contents used, ranging from about 12 kN to 16.9 kN, the air voids level for the entire range of the asphalt cement contents used however, exceeded the recommended range of 4%-7%. As a result, it was not possible to determine an optimum asphalt cement content for this particular mix. Increasing the asphalt cement content to reduce air void level was not a favourable option as the range used is wide enough to encapsulate practical amounts of asphalt cement used in Oman. For this reason, it was recommended to reduce the amount of spent catalyst and redesign the asphalt mix. This step was expected to result in a mix that satisfies the specification requirements. Following that recommendation, the amount of aggregate replacement by the spent catalyst was reduced to 10% by weight of aggregates instead of 20%. The mix design process was then repeated on the modified aggregate structure. The optimum asphalt cement content was found to be 5.5% by total weight of mix. Table 6 shows the mix properties at the optimum asphalt cement content together with the specification requirements. All the properties are in line with the specification requirements. Stability value exceeded the minimum value of 14 kN required by the Oman specifications for wearing course asphalt mixes.

The outcome of the mix design process for the asphalt mixes with the ZCat spent catalyst was more promising. The optimum asphalt cement content corresponding to air void level of 5.5% was found to be 5.6%. The volumetric properties and Marshall parameters corresponding to this asphalt cement content are shown in Table 7. The ZCat mix met most of the Omani specification requirements except for stability which was marginally less than the required 14 kN. Because of that, an attempt was made to reduce the amount of the ZCat catalyst filler from 5% to 4%. The optimum asphalt cement content for this level of spent catalyst was determined to be 4.8% which is lower than that obtained when 5% spent catalyst was used. That indicates a more economical mix. The design parameters corresponding to this optimum asphalt cement content are summarized also in Table 7. Reducing the amount of spent catalyst used resulted in a lower VMA and VFA values, and a slightly lower flow values. The main observation that could be made from the data is the sharp increase of stability values when reducing the amount of spent catalyst by 1%. An increase of about 67% in stability was obtained. This indicates high sensitivity of the asphalt mix to the change of the amount of spent catalyst used as a filler material.

Table 5. Mix Design Results- Ecat Catalyst (20%).

% Asphalt Cement	Stability, kN	Flow, mm	Air Voids, %	VMA*, %	VFA**, %	Density, g/cc
4	11.93	3.72	19.04	26.94	29.31	2.08
4.5	13.60	3.79	17.75	26.68	33.46	2.10
5	14.73	3.98	14.49	26.59	45.52	2.13
5.5	16.87	3.81	13.13	24.78	47.04	2.18
6	14.50	4.05	10.78	24.58	56.14	2.19
Specification Limits	14 kN, minimum	2-5 mm	4.0-7.0 %	14-15%	50-70%	-

* Voids in mineral aggregates

** Voids filled with asphalt

Table 6. Design Parameters at Optimum Asphalt Cement Content of 5.5%- ECat Catalyst (10%).

Design Parameter	Value	Specification
Air Voids	6.0%	4.0-7.0 %
Stability	18.2 kN	14 kN
Flow	3.8 mm	2-5 mm
Marshall Quotient	4.8	-
VMA	18.3%	14-15% min
VFA	66%	50-70%
Density	2.310	-

Table 7. Design Parameters at Optimum Asphalt Cement Content of ZCat Mix.

Design Parameter	5.0% ZCat	4.0% ZCat	Specification
Optimum Asphalt Cement Content	5.6%	4.8%	-
Air Voids	5.5%	5.5%	4.0-7.0 %
Stability	13.8 kN	23 kN	14 kN
Flow	2.84 mm	2.6 mm	2-5 mm
Marshall Quotient (kN/mm)	4.9	8.8	-
VMA	18.5%	16.6%	14- 15%
VFA	70 %	60.9 %	50-70%

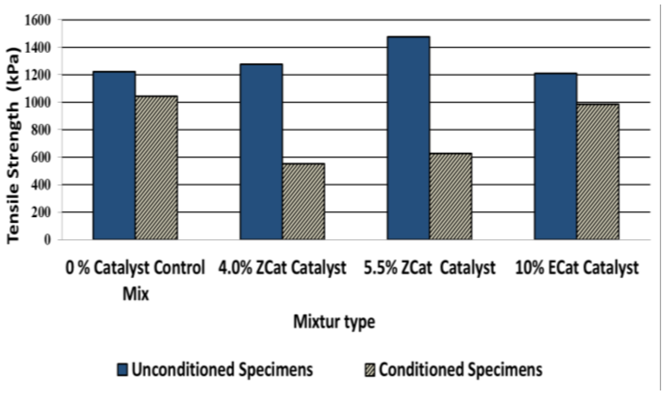

Fig. 2. Indirect Tensile Strength of Asphalt Mixes.

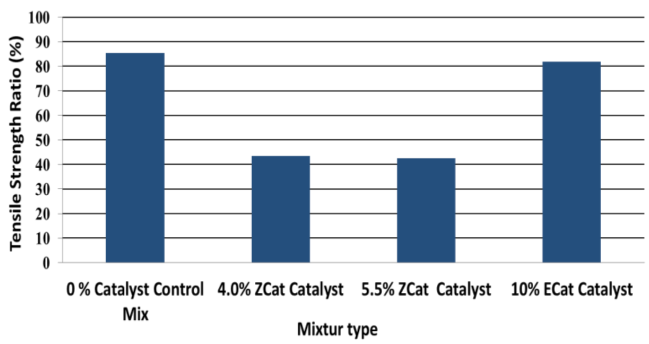

Fig. 3. Tensile Strength Ratios.

Another parameter that is sometimes utilized with Marshall testing is Marshall Quotient (MQ). It is the ratio of the Marshall stability (kN) to Marshall Flow (mm). MQ is an indication of stiffness of the mix and the resistance to deformation in asphalt mixes [10]. A higher value of MQ indicates a stiffer mix that is likely to be more resistant to deformation. Ideally, dense graded mixes should combine high stability with relatively low flow values and hence a high MQ indicating a high stiffness mix and a greater ability to spread the applied load. MQ values are shown together with other Marshall parameters in Tables 6 and 7 for the ECat and the ZCat mixes respectively. The ZCat mix with 4.0% catalyst has the highest MQ value of 8.8 kN/mm indicating a very stiff mix. This value exceeds the range of MQ values usually expected in practice for conventional mixes used in Oman which is between 2.8 and 7.0 kN/mm. Both the 5.0 ZCat mix and the ECat mix have similar MQ values of 4.9 and 4.8 kN/mm respectively. It should be noted that very high stiffness mixes may exhibit lower tensile strain capacity to failure which may suggest that they are more prone to fatigue failure.

Moisture Susceptibility

The presence of moisture in asphalt pavement adversely affects the bond between the aggregate and asphalt cement resulting in the loss of strength and integrity of asphalt mixes. Moisture damage in asphalt concrete pavements can lead to several types of distresses. It is one of the major factors affecting the durability of HMA mix.

The Indirect Tensile Strength (IDT) test has been used as a tool to evaluate the relative quality of asphalt mixes in terms of their resistance to moisture damage. Tensile strength ratios (TSR) are commonly used to measure the stripping potential of HMA mixes. Limiting TSR value of 80% is used by the local specifications here in Oman.

This part of the study explored the potential for moisture damage of asphalt mixes containing spent catalyst. The mixes evaluated for moisture damage were; 0% catalyst control mix, 4% ZCat catalyst mix, 5.5% ZCat catalyst mix, and 10% ECat catalyst mix.

A set of 6 laboratory specimens for each of the four mixes were prepared. Those specimens were compacted to an air void level of 7% ± 1 to match the air void levels expected in the field which are normally in the 6 to 8% range. The set of compacted samples was divided into two subsets of approximately equal void content. One subset was maintained dry and used as a control, whilst the other was moisture conditioned. The tensile strength of each subset was determined by the indirect tensile strength test. The potential for moisture damage is indicated by the ratio of the tensile strength of the wet subset to that of the dry subset. Method of test was conducted as per the standards of the American Society for Testing and Materials (ASTM).

Fig. 2 shows the indirect tensile strength values for the four mix types. Both, the 4% and 5.5% Zcat catalyst mixes have higher unconditioned tensile strength than that of the ECat mix and the 0% catalyst control mix. This indicates that the mixes containing Zcat catalyst are effective in load bearing when they are dry.

Tensile strength results of conditioned specimens show that mixes containing the ECat catalyst have higher tensile strength than both mixes of ZCat catalyst, almost as high as that of the 0% catalyst control mix. Mixes containing 4% and 5.5% of ZCat catalyst both have considerably lower conditioned tensile strengths compared to their dry values indicating a reduced ability to sustain the load when moisture is induced.

Fig. 3 compares the tensile strength ratios of the different mixes. The results show that using 10% of ECat Catalyst as aggregate

Table 8. TCLP Results in ppm of Asphalt Application of ECat and ZCat Spent Catalysts*.

Sample	As	Cr	Cd	Pb	Ag	Hg	Se	Ba
ECat-1	N.D.**	0.031	0.00003	0.049	0.060	N.D.	N.D.	0.334
ECat-2	N.D.	0.032	0.00002	0.044	0.040	N.D.	N.D.	0.104
ECat-3	N.D.	0.025	N.D.	0.056	0.034	N.D.	N.D.	0.096
ZCat-1	N.D.	0.015	N.D.	0.006	0.022	N.D.	N.D.	0.211
ZCat-2	N.D.	0.006	N.D.	0.006	0.040	N.D.	N.D.	0.214
ZCat-3	N.D.	0.010	N.D.	0.006	0.043	N.D.	N.D.	0.217
Regulated Level	5.0	5.0	1.0	5.0	5.0	0.2	1.0	100.0

* all values in mg/L, **Not Detected

replacement produced a tensile strength ratio of 81.8% which exceeds the 80% required for approving its resistance to moisture induced damage. This tensile strength ratio is very close to that of the 0% catalyst control mix which was 85.4%. On the other hand, the samples that contained 4% and 5.5% of the ZCat Catalyst as filler aggregate replacement were proved to be susceptible to moisture damage as it is demonstrated by the values of their tensile strength ratio which were 43.4% and 42.6% respectively. Such low strength ratios make the use of ZCat undesirable from the moisture resistance point of view. It should be noted however, that the indirect tensile strength ratio may decrease due to the relatively higher strength obtained in dry specimens with respect to the conditioned ones as it is the case in the mixes under consideration. The conditioned tensile strength values for the ZCat mixes were about 600 KPa on average which is still a relatively a high strength value that is sometimes obtained for some conventional mixes in their dry state. Moreover, the chemical analysis of the ZCat catalyst indicated a high amount of SiO2 (39.1% compared to only 1.71 % for the ECat). This very fine material with high silica content could well have played a role in increasing the aggregate's affinity to water and possibly lead to the lower moisture resistance.

Environmental Analysis

Environmental characterization of both spent catalysts (ECat and ZCat) was extensively performed in their raw form (i.e. as received) and when utilized in asphalt mix. The toxicity of metals in ECat and ZCat spent catalysts was studied by testing their leachability. This study applied the U.S. Environmental Protection Agency (EPA) Toxicity Characteristic Leaching Procedure (TCLP) to analyze the leachability characteristics. The TCLP as developed by the U.S. Environmental Protection Agency (EPA) was designed to simulate the leaching of metals from the two catalysts in the asphalt mixes. An appropriate extraction fluid for each mix was determined based on the pH of sample as described in TCLP. Dry samples of the mix (10 g) and the appropriate extraction fluid were put with a 20:1 ratio of liquid to dry sample into polypropylene extraction bottles (for metals) and EPA approved borosilicate glass bottles with Teflon-lined caps. The extraction bottles were sealed and then rotated on a specially designed rotator for 18 hours to allow steady-state dissolution and mobilization to occur for small diameter samples. All samples in this study were ground to < 0.85 mm, which is sufficiently small to ensure that steady-state conditions were met. At the end of the 18 hours extraction period, liquid in each bottle was separated from solid phase by vacuum filtration through 0.8 μm glass fiber filter paper. The solid phase was discarded and the pH of the separated TCLP extracts was then measured and all extracts were acidified to a pH less than 2 for long-term preservation. At the end, metal concentrations in the extract were analyzed using Flame, FIAS-MHS and Graphite Furnace Atomic Absorption Spectrometry (AAS) and Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). The samples were analyzed for 8 toxic metals; As, Hg, Se, Cd, Cr, Pb, Ag and Ba. FIAS-MHS was used to analyze As, Hg and Se. Graphite Furnace was used to analyze Cd, Cr and Pb and the flame was used to analyze Ag. The analysis of Ba was done by ICP-OES.

Table 8 shows the TCLP results of ZCat and ECat spent catalysts. According to the obtained results, As, Hg, and Se were not detected in the samples (the regulated levels are 5.0, 0.2 and 1.0, mg/L, respectively). Also, Cd was not detected in many samples but the rest of the samples had Cd concentration in the range from 0.00002 to 0.00003 mg/L which is within the limit (1.0 mg/L). The concentration of the Cr in the samples ranged from 0.006 to 0.032 mg/L which is within the recommended limit of 5.0 mg/L. The concentrations of the Pb in the spent catalysts are 0.006 to 0.056 mg/L, which suggest that the lead concentrations are within the limits (5.0 mg/L). The concentration of Ag ranged from 0.022 to 0.06 mg/L while the maximum limit is 5.0 mg/L. The Ba concentrations ranged from 0.096 to 0.334 mg/L which are well within the acceptable limit (100 mg/L). It was observed that the level of all toxic elements in both ECat and ZCat spent catalysts samples were within the acceptable limits. Hence, it could be safely concluded that the relatively low toxic metals concentrations in the spent catalysts would not cause harmful environment impacts in reuse applications such as asphalt mixes.

Conclusions

This study was carried out to evaluate the potential uses of waste catalysts produced from the process of refining crude oil as a building material in road construction. The chemical analysis indicated that both catalyst types used in this study comprised mainly of Al_2O_3 and SiO_2. The Marshall Mix Design method was followed in designing the asphalt mixes. From a volumetric and stability point of view and for the particular aggregate structure used (surface coarse mix), the ECat catalyst was successfully used as aggregate replacement in the size range of 4.75 mm to 2.36 mm with a recommended amount of 10%, by total weight of aggregate. For the ZCat catalyst, it was possible to use it as mineral filler with a recommended amount in the range of 4%-5%, by total weight of aggregate. The moisture susceptibility evaluation indicated that the ECat mix is superior in their resistance to moisture damage compared to the ZCat mixes. For the amounts of catalyst used in this study, the ZCat mixes failed to meet the moisture resistance requirements of 80% retained strength and hence it is not recommended to be utilized as a filler material. Both types of mixes had a relatively high dry IDT strength values compared to conventional mixes. The environmental characterization performed on the spent catalyst in its raw form (as received) and when incorporated in asphalt mix showed that that the concentration of all toxic metals in the spent catalysts samples that were analyzed did not exceed the allowable limits.

Acknowledgment

The researchers thankfully acknowledge the financial support provided by Oman Refineries and Petrochemical Company (ORPIC) under Sultan Qaboos University Grant No. CR/ENG/CIVL/09/01. The effort of our undergraduate students and laboratory technicians who provided valuable support in conducting this study is also highly appreciated.

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