

# Analysis of Activation Energy and MSCR for Oxidized Asphalts and Their Impact on the Rutting of Pavements

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## Abstract

There have been numerous studies focused on the effect of water on asphalt mixtures, the mineralogy of the aggregates, mastic, and voids. In this research, the effect of water on binder is evaluated in the context of chemical changes, and how such changes impact the material rheological response of asphalt mixtures. This phenomenon has impact on the durability of pavement insomuch as water affects our roads due to prolonged periods of rain and high relative humidity; a typical characteristic of tropical countries. The procedure applied in this research was to submerge 2 mm thick sheets of asphalt in water (of constant controlled properties) for twenty-one (21) months. During that time, the progressive changes in chemical properties, physical properties, and performance of the asphalt were tracked. The results presented in this article are focused on the analysis of the asphalts' activation energy (and the generated change during the period of submersion) in relation to its response to the Multiple Stress Creep and Recovery (MSCR) test: one of the rheological tests that effectively represents the asphalts' behavior under different stress and strain levels.

**Keywords:** Flexible Pavement; Oxidized Asphalt; Activation Energy; MSCR; Moisture Damage; Rutting.

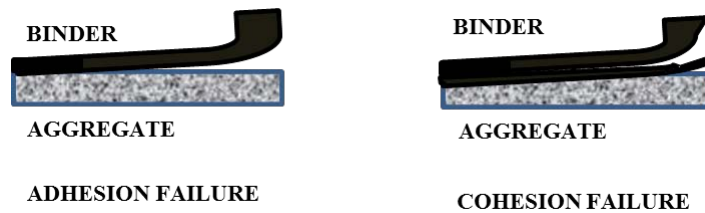
## 1. Introduction

Damage in pavements caused by moisture adversely impacts their functionality, decreasing serviceability and increasing maintenance costs significantly. Evidence of this damage is stripping that is related to cohesion and adhesion [1].

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Adhesion failure is the perfect separation between two surfaces at the interface. Cohesion failure occurs due to internal damage in one of the materials at the interface, usually generating detachment, [2]. The difference between adhesion and cohesion failures is shown in Figure 1.



**Figure 1:** Schematics Showing Adhesion and Cohesion Failure

Past research has shown that asphalt exposed to water for an extended period of time changes its chemical composition [3]. For example, after only three months of exposure, an increase in Carboxyl and Sulfoxide functional groups was observed, generating a structure susceptible to fatigue and rutting. To determine the rate of increase in Carbonyls and Sulfoxides, it is necessary to find the activation energy, which is the minimum energy necessary for a change or chemical reaction to occur in a material. Pavements exposed to traffic loads and environmental effects, such as rain or humidity, gradually deteriorate. The intensity of such deterioration depends on: pavement structure, material properties, the difference between adhesion and cohesion failures, and the response of each of the components of the asphalt mixture. In other words, mastic, voids, aggregates and asphalt within the asphalt mixture all contribute to deterioration, however, each one does so in different ways and by differing amounts. Therefore, it is the goal of this research to extend the useful life of pavements through studying these effects. One of the benefits of modern pavement engineering is the possibility to analyze asphalts and (according to their response at different temperatures, loading frequencies, and deformations) predict their performance in the asphalt mixture. Although the role of aggregates is essential, the analysis of binders through some tests such as MSCR, as in [4,5,6], indicates the susceptibility that pavement can have with respect to effects generated by traffic, such as rutting

## 2. Materials and methods

### 2.1. Test Plan

This experiment included not only the analysis of the properties of eight samples of asphalt with different levels of oxidation, but also wheel tracking tests in order to measure the performance of each mixture manufactured with oxidized asphalt. See Table 1.

#### 2.1.1. Asphalt

The changes in the mechanical properties of the binder after water conditioning for extended periods of time (i.e., S0, S3, S6, S9, S12, S15, S18 and S21 months) were studied in this research. Sheets of 80-100 (1/10 mm) penetration grade asphalt (of 2mm thickness) were conditioned resting on 4mm thick sheets of glass. The length and width of each sample was 45x45 cm (as shown in Figure 2). These samples were submerged in potable water at 16°C during 21 months in different containers made of natural glass fiber to avoid any water

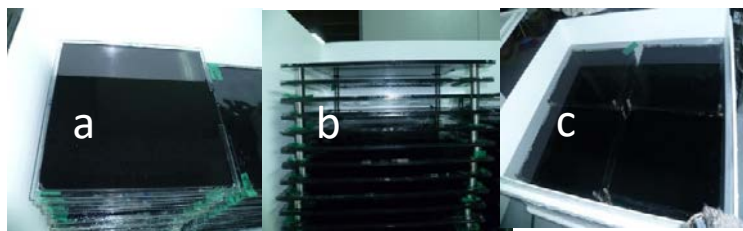
contamination. The test plan for this experiment is indicated in Table 1. The rheological analysis was replicated 10 times with 200 measurements for each test. The chemical and physical measurements were replicated 6 times for each test.

**Table 1:** Test Plan (Asphalt Properties Analysis)

Binder	Water Control	Physical Properties	Rheological Properties	Chemical Properties	Dynamic Properties
	Constant	Variable	Variable	Variable	Variable
from S0* to S21**	Dissolved Oxygen	Penetration at 25°C(1/100mm)	Complex Modulus  G* (Pa)	Asphaltenes (%)	Wheel Tracking
	Sulphates	Softening Point (T°C)	PG max (°C)	Resins(%)	
	Chlorides	Penetration Index	PG (PAV) (°C)	Saturated(%)	
	Hydrogen Potential-PH	Ductility (100+cm)	PG (water) (°C)	Aromatic(%)	
	Conductivity	Flaming Point (T°C)	Jnr,3.2 (1/kPa)	Carboxyls	
	Turbidity	Ignition Point (T°C)	Elastic Recovery	Sulfoxides	
	Total Alkalinity	Brookfield Viscosity at 135°C(Pa.s)	Traffic level,(Heavy)	lc-Colloidal Instability Index	
	Acidity	Specific Gravity		ls-Colloidal Clasification	
	Hardness				

\*Original condition of asphalt

\*\*Submerged asphalt (S). The number indicates how many months the asphalt was exposed to the water oxidation



**Figure 2:** Placement of the asphalt submerged in containers with water: (a) samples of 2mm thick sheets of asphalt on glass (b) placement of the samples (c) submerged samples

This article presents the changes that occurred in the asphalt in regard to Activation Energy, the MSCR and its performance. The analysis charted of the asphalt was trimestral during the complete period of immersion (21 months).

### 2.1.2. Water

In such an experiment, where potable water is used, an important consideration is water quality and the magnitude of suspended and dissolved particles. To decide on water quality, a comparison was made between laboratory test results and data from the rainwater database of the Hydrology Institute of Meteorology and Environmental Studies-IDEAM from Colombia between 1999 and 2010. The results of this comparison indicated that the acidity, conductivity, dissolved oxygen, and sulfate content of rainwater was not significantly different from potable water. The properties of water used for asphalt submersion are shown in Table 2.

### 2.1.3. Asphalt Mixture

The asphalt mixture was made based on the *Superpave*<sup>®</sup> process, level 1 and the maximum nominal size of the

aggregate was 19 mm. The results are shown in Table 3.

**Table 2:** Properties in the water at 16°C

Parameter	Name	test			Measured points	Overage	Desvest	Cov
		1	2	3				
DISSOLVED OXYGEN	SM 4500 -O C	10,00	8,00	10,00	27	9,111	1	0,08
		8,80	9,20	8,40				
		9,60	8,80	9,20				
SULPHATES	SM 4500-SO4 E	1,22	1,25	1,46	27	1,369	0	0,18
		1,50	1,31	1,52				
		1,15	1,87	1,04				
CHLORIDES	SM 4500-CL-B	13,00	10,00	11,00	27	12,000	2	0,15
		12,00	12,00	13,00				
		7,33	7,15	6,95				
PH (potential of hydrogen)	SM 4500-H+B	7,23	7,05	7,15	27	7,070	0	0,03
		7,24	6,70	6,83				
		54,80	53,50	54,80				
CONDUCTIVITY	SM 2510 B	55,80	53,20	52,40	27	50,733	7	0,13
		52,10	45,80	34,20				
		0,80	0,80	0,80				
TURBIDITY	SM 2130 B	0,80	1,20	1,10	27	0,911	0	0,17
		0,80	0,90	1,00				
		12,00	14,00	12,00				
TOTAL ALKALINITY	SM 2320 B	12,00	14,00	16,00	27	14,000	2	0,12
		14,00	16,00	16,00				
		10,00	8,00	8,00				
ACIDITY	SM 2310 B	10,00	8,00	10,00	27	8,667	1	0,16
		10,00	8,00	6,00				
		40,00	36,00	30,00				
HARDNESS	SM 2340 C	30,00	24,00	22,00	27	31,556	6	0,18
		34,00	34,00	34,00				

**Table 3:** Asphalt Mixture Design (maximum size 19mm)

Asphalt Content (%)	Air Voids (%)	VMA (%)	VFA (%)
5.7	4.1	14.2	71.6

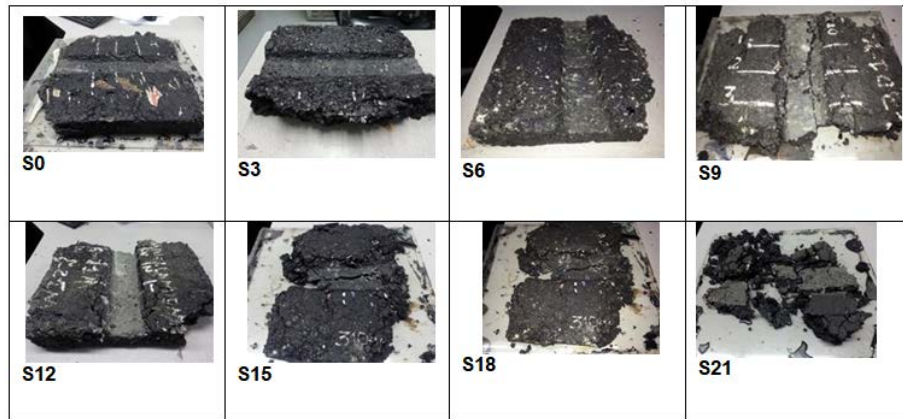
**2.1.4. Wheel Tracking Test**

In this experiment, 13 tons of force was applied to the asphalt mixtures through a wheel and a resultant pressure of 0.662MPa was calculated at the point of contact. The rotation of the wheel was set to 42 r.p.m above the briquette (of dimensions: 300mm x 300mm x 50mm) at 60 ° C. See Figure 3.



**Figure 3:** Wheel Tracking Test at 60°C

Plastic deformation increased dramatically as the oxidation time of the asphalt increased, see Table 4. Figure 4 shows the total disintegration of the asphalt mixture for each period of oxidation.



**Figure 4:** Plastic deformation for asphalt S0 to S21

**Table 4:** Plastic deformation

Asphalt	S0	S3	S6	S9	S12	S15	S18	S21
<b>Plastic deformation (mm) at 105 minutes</b>	19,7	10,6	8,5	7,4	9,42	11,7	11,97	17,11

### 2.1.5. Activation Energy

Activation energy, AE, is defined as the minimum energy needed for a change or chemical reaction to occur in a material. For the submerged asphalt samples, energy increased with respect to time due to the rise of polar molecules within the asphalt. From the analysis of background AE it was discovered that, for different asphalts, the AE varies between 44 kJ/mol and 90 kJ/mol, [3]. The following example presents calculations of AE for asphalt sample S0.

The activation energy, see Figure 5, was calculated based on the Arrhenius equation, equation (1).

$$K = A * \exp\left(-\frac{E_a}{RT}\right) \quad (1)$$

Where:  $K$ : Kinetic constant

$A$ : Specific constant for each reaction.

$E_a$ : Activation Energy J/mol

$R$ : Universal constant of gases.

$$8,3143 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

T: Absolute Temperature (°K)

Applying the laws of logarithms:

$$\ln \frac{K}{A} = -\frac{E_a}{RT}$$

$$\ln K - \ln A = -\frac{E_a}{RT}$$

$$\ln K = \ln A - \frac{E_a}{RT} \tag{2}$$

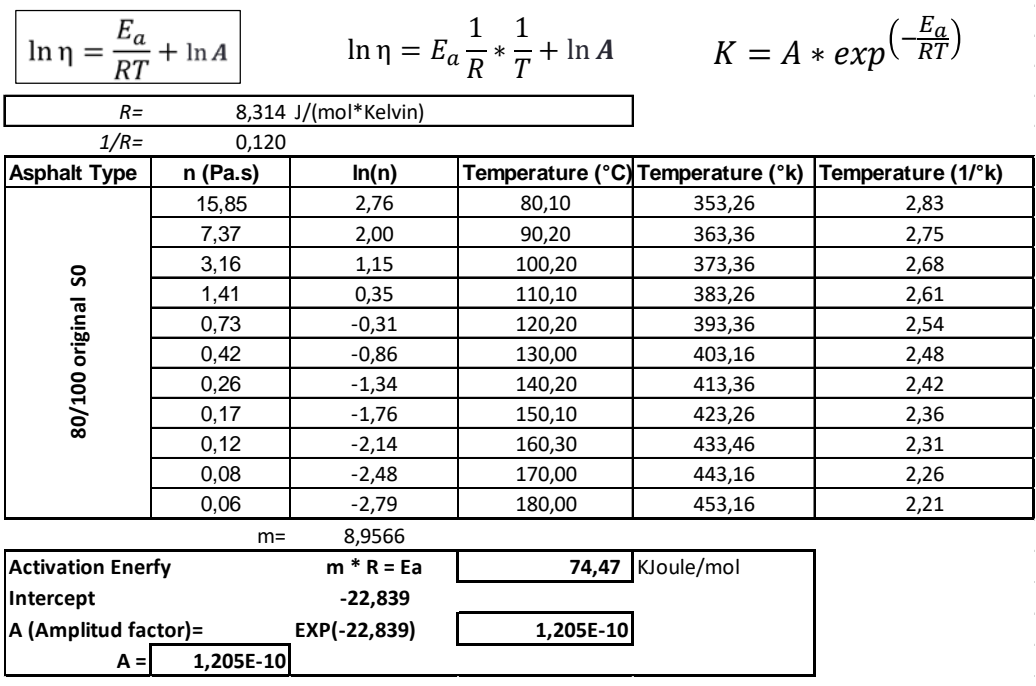
ln K = Temperature Dependent Variable,

$\frac{1}{T}$  = Independent variable

$\frac{E_a}{RT}$  = Slope of the linear graph ln(η) vs. 1/K

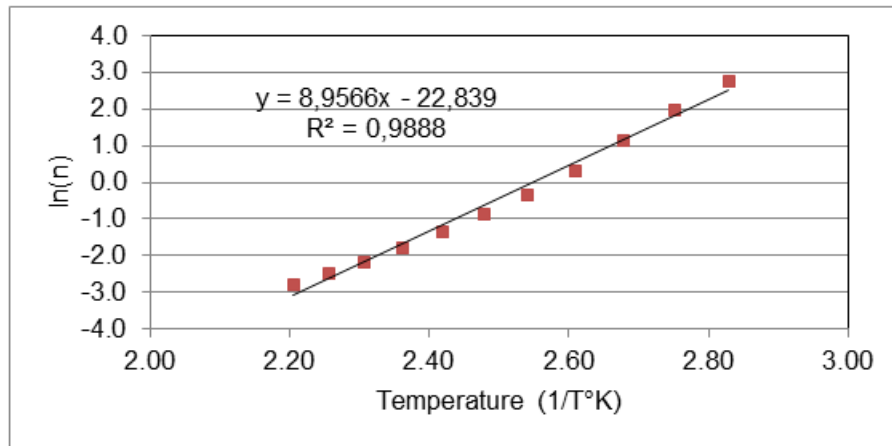
ln A =Independent term or intercept of the linear graph, Example of Activation Energy calculation for the original asphalt, S0.

**Arrhenius equation**



**Figure 5:** Analysis and calculation of the activation energy from the Arrhenius Equation, asphalt S0.

Based on the data in Figure 5 , the graph of ln(η) vs. 1/T, in Figure 6 was constructed.



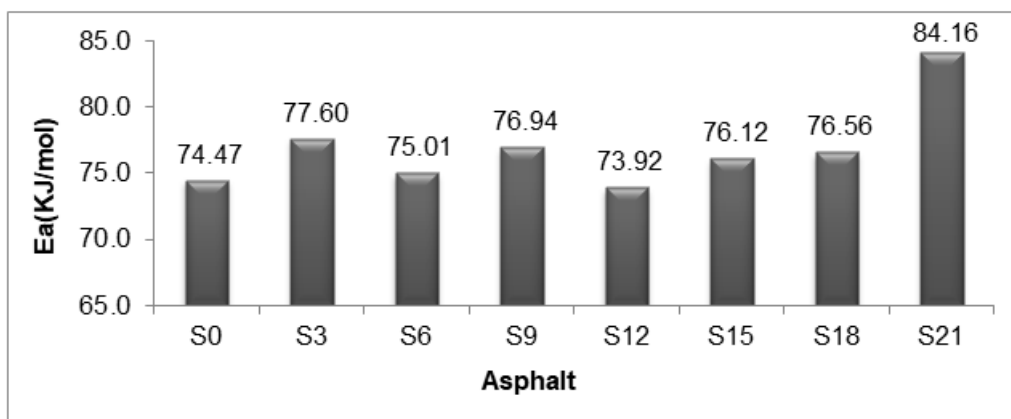
**Figure 6:** Activation Energy for all periods of oxidation

$$E_a = (\text{Slope of the linear Graph}) \times K$$

$$E_a = 8,9566 * 8,3143 \text{ J}/(\text{mol} * \text{K})$$

$$E_a = 74,465 \text{ kJ}/\text{mol}$$

In this way, the calculation of  $E_a$  was interpolated for all months of submersion. In this experiment, the maximum AE was found in asphalt sample S21 at 84,16 KJ/mol. This value is very close to the maximum reported so far [3], which indicates that after approximately 21 months, asphalt experiences a maximum level of oxidation. See Figure 7.



**Figure 7:** Activation Energy (EA) for each oxidation period

### 2.1.6. Multi Stress Creep and Recovery-MSCR

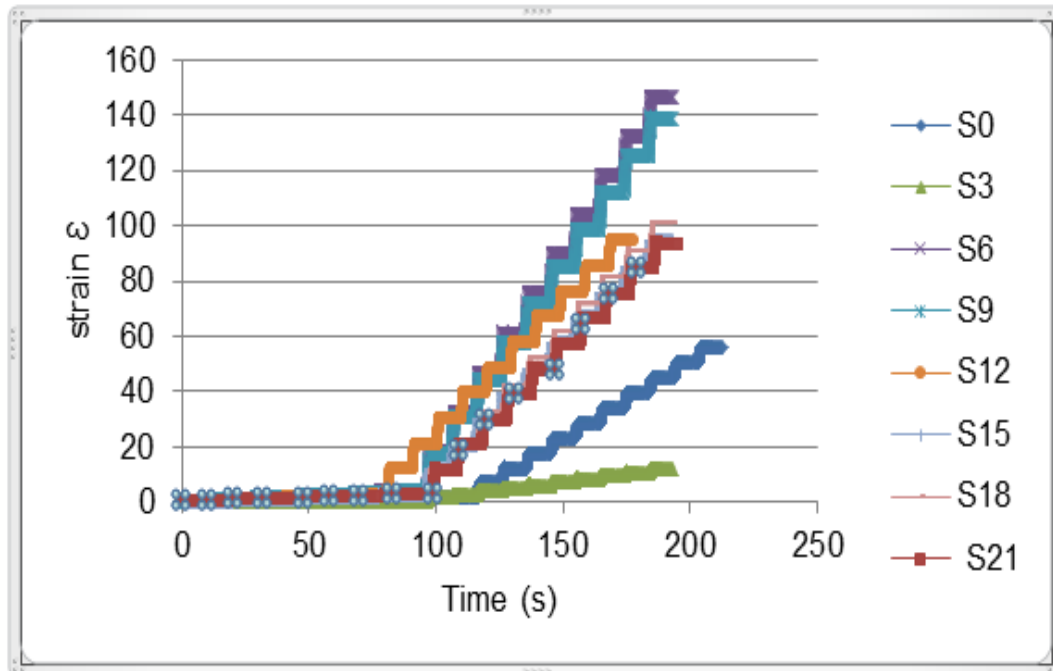
The MSCR and the percentage of recovery are two of the setting that are calculated using measured tension in different cycles of strength, [7], in order to analyze the response of asphalt under traffic loads. The measurement of the Multiple Stress Creep Recovery–MSCR test of the submerged asphalt samples was

performed for the maximum Performance Grade-PG of each asphalt sample with the purpose of evaluating the permanent and recovered strain, in accordance with [7] which says, “With the new MSCR specification, the binder testing is done at the high environmental temperature that the pavement is expected to experience. If the climate grade is a PG 64 or PG58, you would do all high temperature testing at 64°C or 58°C. If heavy traffic is expected the specification requirement is changed, i.e. a lower Jnr value is required to reflect the increased stress the pavement will experience, but testing is still done at say 64°C for a PG 64 climate.” Table 4 indicates the values of the complex modulus  $[G^*]$  of each sample for the maximum PG used in the MSCR test. See Table 5.

**Table 5:** Value of module  $|G^*|$  a 64°C for all asphalts

S0	S3	S6	S9	S12	S15	S18	S21
933	1261	1343	1375	1689	2158	2147	1382

As for the variation of accumulated deformation, after each period of submersion it was observed that asphalt sample S3 became more and more rigid and, therefore, decreased its accumulated deformation over time. For submersion periods S6 to S18, the accumulated deformation gradually increased, however, asphalt sample S21 broke this trend by exhibiting a decrease. S0 and S3 were tested at 58°C. S6 through S21 were tested at 64°C. See Figure 8.



**Figure 8:** Multiple Stress Creep and Recovery (MSCR) for asphalts from S0 to S21.

Table 6 shows the change in creep compliance unrecoverable  $J_{nr}$  and the elastic recovery of each asphalt sample.



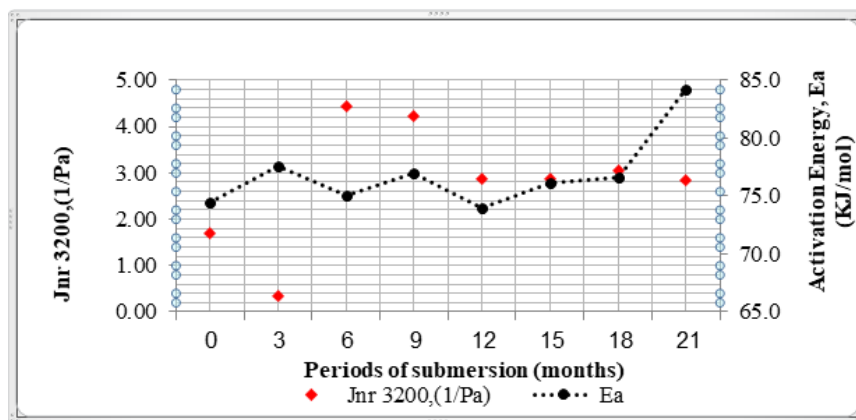
**Table 6:** Results of MSCR trial at maximum PG temperature for each asphalt

Asphalt	Level of Stress 0,1 kPa <sup>-1</sup>		Level of Stress 3,2kPa <sup>-1</sup>		Rdiff	Jnr,diff
	Jnr,0,1 (1/kPa)	Elastic recovery	Jnr 3,2(1/kPa)	Elastic recovery		
S0	1,574	0,36	1,703	0,000	894	8,16
S3	0,333	15,97	0,359	11,410	29	7,54
S6	4,176	0,00	4,450	0,000	-64	6,55
S9	3,929	0,00	4,220	0,000	-77	7,42
S12	2,606	0,68	2,870	0,000	654	10,16
S15	2,629	0,00	2,862	0,000	-585	8,87
S18	2,820	0,00	3,061	0,000	-335	8,55
S21	2,570	0,07	2,838	0,000	5368	10,46

The Jnr values obtained for each asphalt sample are related to the traffic levels for which the asphalt would have the best response in terms of permanent deformation. See Table 7.

**Table 7:** Correlations between Jnr and adequate levels of traffic

Level of traffic	J <sub>nr</sub> (kPa <sup>-1</sup> ), maximum	ESALs and speed
standard (S)	4	< 10 million and standard speed (V <sub>M</sub> > 70 km/h) <sup>a</sup>
heavy (H)	2	Between 10 and 30 million of slow traffic (20 < V <sub>M</sub> < 70 km/h)
Very heavy (V)	1	> 30 million of stopped traffic (V <sub>M</sub> < 20 km/h)
Extremely heavy (E)	0,5	> 30 million of stopped traffic (V <sub>M</sub> < 20 km/h) areas of heavy traffic stopped or ports



**Figure 9:** Comparison of Jnr and activation energy, AE, for all samples with respect to time.

The activation energy for all submersion periods showed uniform changes ranging from 74.47 to 84.16 KJ / mol. There were abrupt decreases to the Jnr of the asphalt during the first 3 months of submersion, however, after a sharp increase until month 6, from month 6 to 12 it gradually decreased until reaching a level at which it stayed relatively constant during the remaining months. Figure 1 shows the trends of Jnr and AE with respect to time.

### 3. Conclusions and Recommendations

During the period of submersion, physical, rheological and chemical monitoring was done every three months to study changes to the asphalt caused by water. Additionally, some tests were done to compare the performance of common asphalt mixtures with each sample of asphalt (for S0 through S21). However, in this article only the results from the MSCR test and the AE test are analyzed and discussed. In total, eight periods of submersion were analyzed, taking into account the initial conditions of the material. The properties of the conditioning binders in water: S0, S3, S9, S12, S15, S18 and S21 are presented in Table 8.

**Table 8:** Asphalt properties from S0 to S21

Asphalt	TEST (average)				
	Flash Point Cleveland cup	Softening Point	Brookfield Viscosity	Penetration	Ductility
Standard	ASTM D 92	ASTM D36	ASTM D4402 06	ASTM D5	ASTM D113
S0	50,6	50,6	0,381	83,2	144,5
S3	52,0	52,0	0,452	58,7	106,8
S6	53,0	53,0	0,453	48,4	101,7
S9	53,0	53,0	0,394	43,0	93,7
S12	52,2	52,2	0,527	47,1	95,1
S15	52,7	52,7	0,564	46,6	94,2
S18	53,0	53,0	0,584	46,5	93,2
S21	53,3	53,3	0,619	46,5	92,5

Activation energy is the minimum energy required to generate a chemical reaction or change in a material. In this experiment, the activation energy of the asphalt samples increased by 13% after 21 months of submersion. According to international literature, AE values vary from 44 kJ / mol to 90 kJ / mol (Coe & Cui, 2003) for different asphalts. It is therefore concluded that maximum oxidation of the asphalt samples was realized after 21 months. However, in the recommendations for this research it is suggested to perform experimental water diffusion tests on the asphalt.

The maximum non-recoverable plastic strain of the MSCR test was obtained after three months of submersion. This result was consistent with the physical and chemical results of asphalts sample S3 and is further supported by the fact that the strongest changes of the submerged asphalt were observed in the first three months.

For a deformation of 10% in the MSCR trial, the highest accumulated deformation was obtained after three months of submersion. Given the observation of the tendencies of penetration and dynamic trials, an abrupt decrease in asphalt quality is realized during this time. All submerged asphalt samples didn't exhibit elastic recovery, making them more susceptible to rutting. The only exception was asphalt sample S3, which

demonstrated the worst values of quality and performance for all tests. The variation of the complex modulus of all asphalt samples with respect to temperature exhibits an oscillatory behavior. All asphalt samples became more susceptible to rutting, and stripping as the submersion time increased. This research evidences the physiochemical and rheological changes that asphalt is subjected to because of water, either in liquid (rain or stagnant water) or vapor (moisture) form. This is a typical condition in tropical countries, where frequent rain and high temperatures are common. In accordance with the maximum activation energy and the MSCR test results for changes to the asphalt samples, it is necessary to highlight the variation of performance with respect to traffic levels. Initial testing of the asphalt (S0) yielded performance levels acceptable for heavy traffic but after three months, when the deterioration from oxidation was evident, performance levels were only acceptable for standard traffic. This implies that it is necessary to consider oxidation in pavement design since, currently, only the load function of growth rate and the type of pavement are taken into consideration.

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