

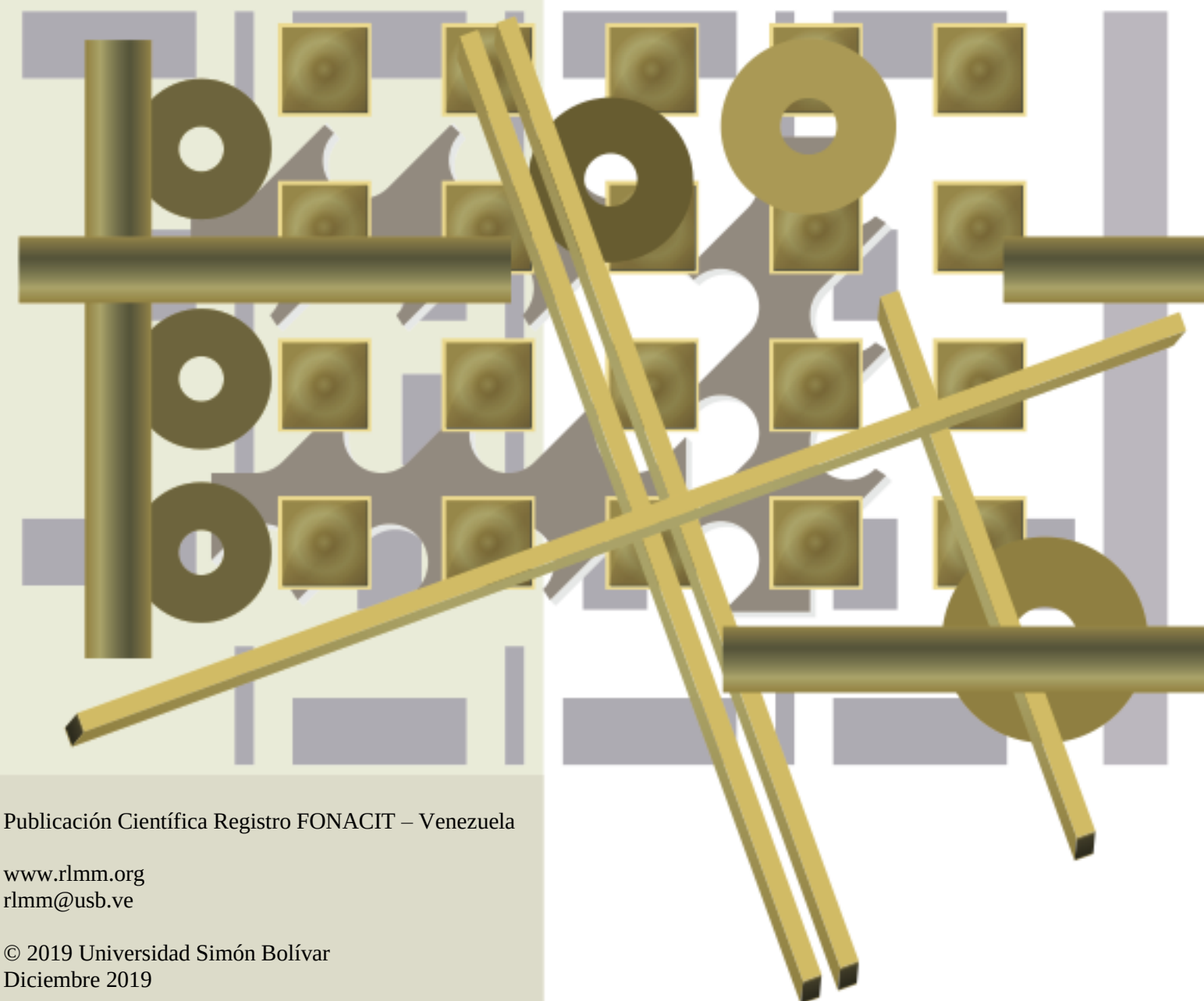


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EDITORIAL

Nos complace presentar el presente **número 1** (segundo semestre del **año 2019**) del **volumen 39** de la Revista Latinoamericana de Metalurgia y Materiales (RLMM). En este número se publican **05 artículos regulares** de autores iberoamericanos.

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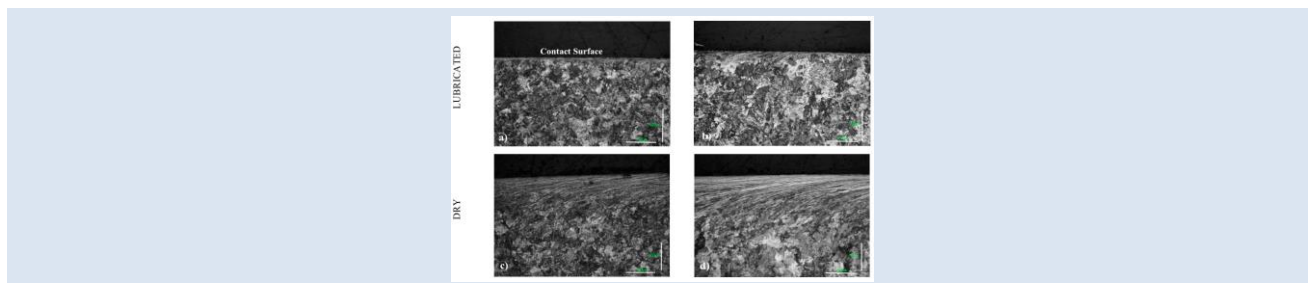
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TWIN-DISC ASSESSMENT OF THE EFFECT OF TOP-OF-RAIL FRICTION MODIFIERS ON THE TRIBOLOGICAL RESPONSE OF ER8-R370HT PAIRS FOR USE IN WHEEL-RAIL SYSTEMS

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ABSTRACT

This paper studies the effect of the addition of top of rail - friction modifiers (TOR-FM's) on the tribological response of a rolling-sliding pair submitted to similar conditions to those found in commercial wheel-rail systems. The tests were conducted in a wheel-rail contact simulator (twin-disc machine) and the samples were extracted from worn wheels and rails provided by Metro de Medellín (Colombia). The tests were carried out using two Friction Modifiers. Dry tests were also performed for reference purposes. TOR-FM1 was a commercial friction modifier and TOR-FM2 was developed in the laboratory for the operating conditions of Metro de Medellín. The Hertzian contact pressure was 1 GPa and the average roughness (R_a) before the tests was fixed at 1.3 μm . The addition of friction modifiers at the interface reduced the Coefficient of Friction (COF) when compared to the dry condition, improved the surface quality and reduced the depth of the deformed material layer under the contact surface.

Keywords: Top-of-Rail Friction Modifiers, Wheel-rail contact, Wear rate, Creepage.

EVALUACIÓN MEDIANTE ENSAYOS DISCO-DISCO DEL EFECTO DE LA ADICIÓN DE MODIFICADORES DE FRICCIÓN SOBRE LA RESPUESTA TRIBOLÓGICA DE UN PAR ER8-R370HT PARA USO EN SISTEMAS RUEDA-RIEL

RESUMEN

El presente trabajo estudia el efecto de la adición de modificadores de fricción para uso en la cabeza del riel (TOR-FM's) sobre la respuesta tribológica de un par rodante-deslizante sometido a condiciones similares a las encontradas en sistemas ferroviarios comerciales. Los ensayos fueron llevados a cabo en un simulador rueda-riel tipo disco-disco y las probetas fueron extraídas de ruedas desgastadas y rieles proporcionados por el Metro de Medellín (Colombia). Los ensayos fueron realizados con dos tipos de modificadores de fricción y se estudió también la condición en seco como referencia. El TOR-FM1 fue un modificador de fricción comercial y el TOR-FM2 fue desarrollado en laboratorio para condiciones de operación del Metro de Medellín. La presión de contacto Hertziana fue de 1 GPa y la rugosidad promedio (R_a) inicial fue fijada en un valor de 1.3 μm para todos los ensayos realizados. Se pudo encontrar que la adición de modificadores de fricción en la intercara favorece la reducción del coeficiente de fricción (COF) comparado con las condiciones en seco, mejora la calidad superficial y reduce la profundidad de la capa de material deformado bajo la superficie de contacto.

Palabras Claves: Modificadores de fricción TOR, Contacto rueda-riel, Tasa de desgaste, Porcentaje de deslizamiento.

1. INTRODUCTION

The use of lubricants in a rail-wheel interface improves the performance of railway systems concerning wear and noise [1]. Over the years, the maintenance cost of railway systems has significantly increased due to wear of rails and wheels. In 1980, the United States of America (USA) spent US\$ 600 million per year in rail changes [2], the European Union reported 300 million euros for the rail maintenance [3] and in 2002, the USA reported 2 billion dollars in maintenance expenses [4]. Ready et al [5] showed that maintenance expenses are higher for non-lubricated curves when compared to lubricated curves since the use of the lubricants with constant or intermittent application in the contact area leads to effective reductions in maintenance expenses.

Friction and wear control is achieved in the field by the application of a third material at the rail/wheel contact zone. The application of lubricants is done at the gauge face (GF) in the wheel flange contact, while friction modifiers (FM) are used in the top of the rail (TOR) to reduce squealing noise and surface damage related to corrugation, rolling contact fatigue and wear [6]. The application of TOR-FM also allows reducing and optimizing the level of Coefficient of Friction (COF) to keep safe operation conditions [6]. Ready et al [5] showed that the addition of a third material to the contact zone in the wheel-rail contact leads to wear rate reduction particularly in tight curves. For instance, in curves with curvature radius smaller than 200 m the wear rate is reduced up to five times. Comparable results were shown by Tameoka et al [7] who studied the difference between tests under dry conditions and with addition of TOR-FM's and greases. The authors found that the COF strongly depends on the lubrication conditions, and specifically, that the addition of a TOR-FM keeps the COF constant while lubricants and greases invariably lead to progressive reductions in friction to values low enough to prevent safe and efficient operation of railway systems during braking and traction [8].

On the other hand, when the creepage in the rail/wheel contact interface increases, the frictional force also increases. In rolling-sliding contact, there are two zones in the contact area: the adhesion zone (stick) and the slip zone. In the stick zone the velocity of the two surfaces is very similar (typical of pure rolling) but as creepage increases a new

zone (slip zone) appears where there is a significant difference between the speed of the surfaces of each body in contact. When the creepage increases, the stick zone reduces and finally, the contact behaves theoretically as pure sliding [9].

In practical terms, the most important rail wear mechanism in the field is controlled abrasion generated by rail grinding. However, the fatigue life of rails is highly dependent on the COF as can be explained by the shakedown diagram [10]. If the creepage and the COF are controlled, the emergence of initial cracks can be significantly delayed [6]. Accordingly, if the COF is controlled by the addition of a TOR-FM, the surface damage can be hindered as well as the wear rate induced by rail grinding.

The variation of COF under different values of creepage when a FM is added to the contact surfaces, as well as the saturation value when the COF achieve a value similar to the 100% sliding test, constitute key information before testing the rails and wheels in the field, since the COF between rail and wheel affects the surface damage and the amount of plastic deformation at the sub-surface.

In this work, twin-disc tests were performed to determine the tribological behavior of wheel and rail materials as a function of the creepage. The tests were performed in the presence of friction modifiers and the results were compared to those obtained under dry condition. After the tests the mass losses were determined, and all the samples were submitted to worn surface inspection, microstructural analysis of the deformed layer and microhardness tests.

2. EXPERIMENTAL PROCEDURE

2.1 Samples

All the samples were extracted from wheels and rails provided by Metro Medellin. Rail samples were extracted from the head of the rail and for the wheel samples a region close to the contact band was targeted. Figure 1 shows the description of the extraction zones and the samples' size and shape. Table 1 shows the chemical composition of rail and wheel materials and Figure 2 shows the microstructure of the samples. The rail material is classified as hardened R370HT rail steel according to UNE-EN 13674 standard [11] and the wheel material as ER8 wheel steel according to UNE-EN

13262 standard [12]. The microstructure was analyzed using Scanning Electron Microscope (SEM) JEOL 5910LV and Light Optical Microscope (LOM) Nikon Eclipse Ci-L/S. The

samples were polished using a standard procedure described in ASTM E3 standard and etched using Nital 2%.

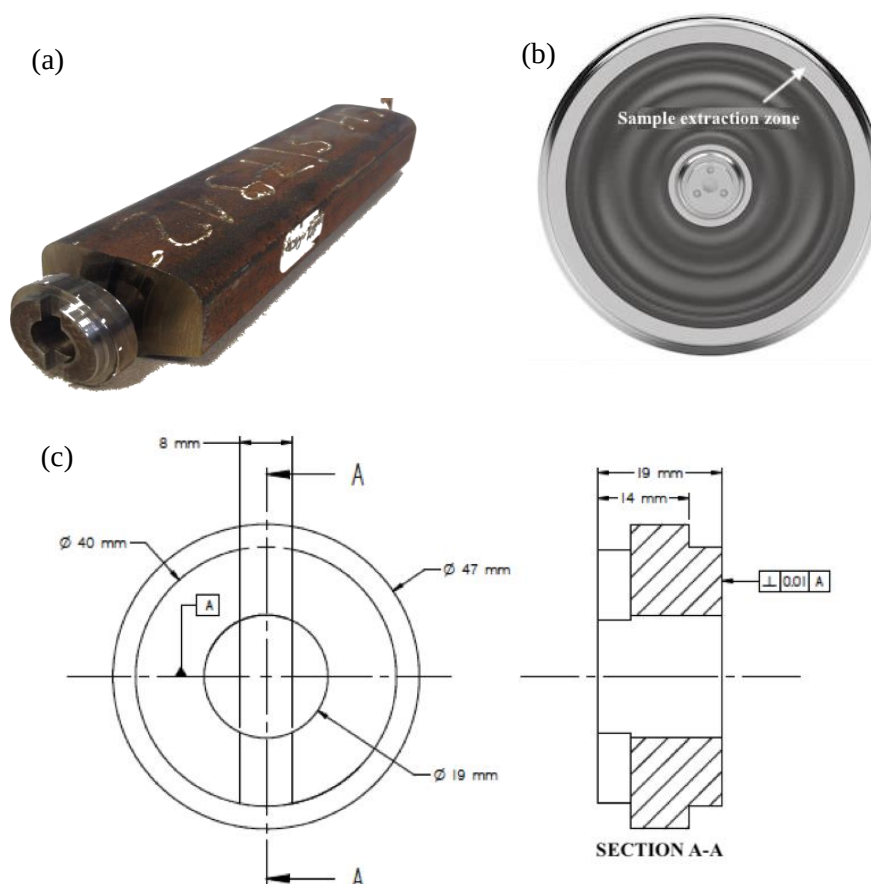


Figure 1. Zones of extraction of the samples from rails and wheels for twin-disc tests (a, b) and shape and dimensions of the samples (c).

Table 1. Chemical composition of rail and wheel materials measured by Optical Emission Spectrometry (BRUKER Q8 MAGELLAN). All the measurements were performed on surfaces polished with emery paper n. ASTM 600 with no chemical etching.

Element (wt. -%)	C	Si	Mn	S	P	Ni	Cr	Mo	Cu
Rail	0.772	0.454	1.213	0.016	0.015	0.020	0.082	0.015	0.019
Wheel	0.540	0.232	0.745	0.004	0.014	0.114	0.172	0.050	0.225

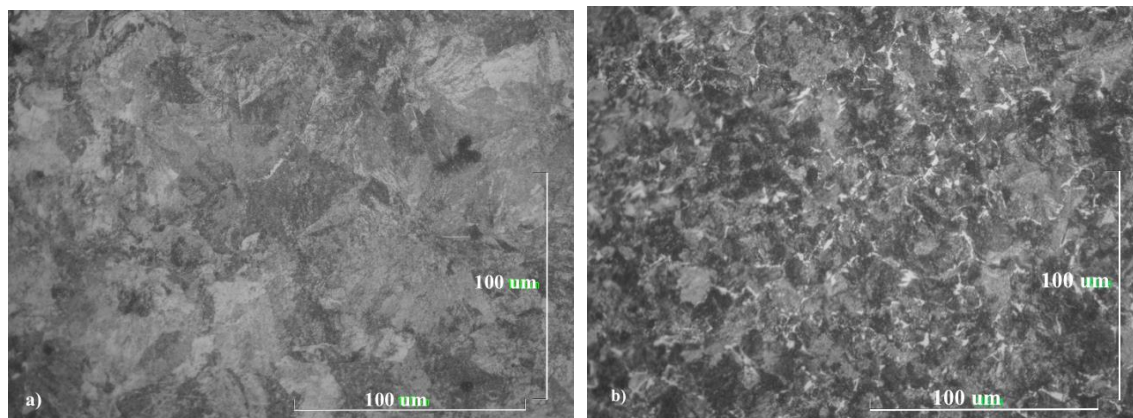


Figure 2. Microstructure of a) Rail sample (pearlite) and b) Wheel sample (pearlite + 7% ferrite).

The surface of the samples was prepared with similar processes to those used in the Metro de Medellín for maintenance purposes. The wheel samples were lathe turned whereas for the rail samples a grinding setup was used. The initial R_a of the samples ($R_a = 1.3 \mu\text{m}$) was fixed for all the experiments by controlling either the lathe turning conditions (wheel specimens) or the grinding setup parameters (rail specimens). R_z roughness parameter was also measured at the beginning of the tests and the value obtained is presented in Table 2 for both wheel and rail samples. The roughness measurements were performed with a Mitutoyo SurfTest SV 3000 station profilometer.

Table 2. Roughness parameters of the samples before the tribological tests.

Sample	R_a (μm)	R_z (μm)
Rail	1.3	3.6
Wheel	1.3	1.9

2.2 Friction Modifiers physical properties

Figure 3 shows the viscosity and shear stress properties of the TOR-FM's used in the tests as a function of the shear rate.

Both friction modifiers used in this work are composed of an oil base, thickeners and solid lubricants. In the case of TOR-FM1 the base is an Ester while in TOR-FM2 it is a vegetable oil. The viscosity and shear stress of the two friction modifiers are shown in Figure 3 as a function of the shear rate. The response at low shear rates is very similar for both TOR-FM's while for high shear

rates the shear stress of TOR-FM2 is lower than that of TOR-FM1.

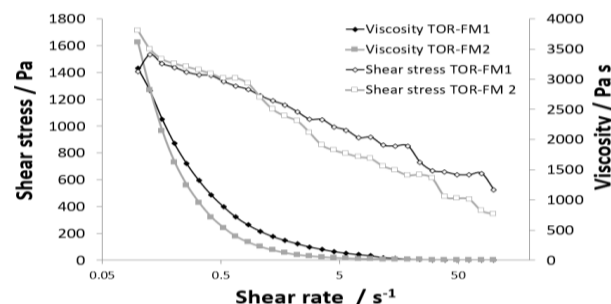


Figure 3. Viscosity and shear stress as a function of shear rate for the friction modifiers studied in this work.

2.3 Tribological tests

All the tests were carried out in a twin-disc testing machine shown schematically in Figure 4. The wheel and rail samples are mounted in two parallel shafts driven by independent electrical motors to induce and control the proper creepage during the tests. A hydraulic actuator applies the normal load to the samples and a torque transducer is used to measure the friction force generated at the contact surface. The tests were carried out under dry and lubricated conditions. For lubricated tests, two TOR-FM's were used (TOR-FM1 and TOR-FM2), being one of them (TOR-FM2) specifically developed for the operating conditions of Metro de Medellín [14]. The contact pressure used was 1 GPa and the values of creepage were selected to obtain a complete creep curve to understand the behavior of the friction modifiers under different conditions. Curves with different creepages (0.8, 3, 5 and 7%) were obtained and the COF was measured. All the tests were carried out up to 6500 cycles. A different

pair of samples (rail and wheel) was used for each tribological test and three replicas were obtained for each testing condition, i.e. Dry, TOR-FM1 and TOR-FM2.

In lubricated tests, the addition of the TOR-FM only started after initial 500 dry cycles (running-in stage). 0.05 g to 0.07 g of TOR-FM were manually added

to the contact area every 500 cycles with the aid of a brush. The same method has been used previously with success to study the effect of FM's on Rolling Contact Fatigue [11, 15].

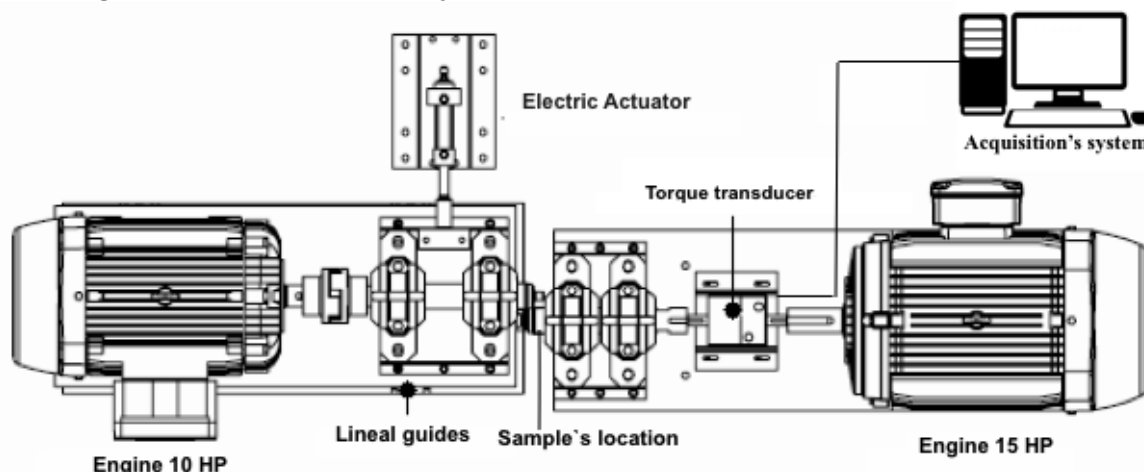


Figure 4. Schematic of the twin-disc testing machine used for all the experiments.

At the end of the tests the worn surfaces were inspected to identify the main wear mechanisms, and cross sections of the samples submitted to extreme conditions (0.8% - 7% creepage) were used for microstructure analysis and micro-hardness measurement with focus on the sub-surface deformed layer.

3. RESULTS AND DISCUSSION

3.1 Variation of COF with testing time

Figure 5 shows the variation of COF with the number of cycles for dry tests. The COF increases with the creepage reaching a stable value after 600–700 cycles approximately. For high creepages the COF is always between 0.55 and 0.60. For low creepages (0.8%) the COF value is close to 0.20. The tangential force in the stick region reaches lower values compared to those in the slip zone, therefore when the creepage increases a difference in the COF can be observed due to the increase in the size of the slip zone in the contact area. Hence, the values of the COF vary for each creepage tested [10]. For high creepages (between 3% and 7%), the value of COF decreased after 4000 cycles approximately, which has been associated to the formation of stable oxides on the surface, which act

as solid lubricants [16,17].

In lubricated tests three stages are clearly observed as a function of testing time. In zone 1 (the TOR-FM has not been added yet) the COF increases until the traction force is stabilized; in zone 2 the COF decreases quickly due to the addition of the TOR-FM, and in zone 3 a constant COF value under 0.10 for all creepages is reached (Figures 6 and 7). As the addition of the TOR-FM is intermittent, the COF plots show some periodicity which is related to the actual time that the boundary layer of TOR-FM is stable on the surfaces.

3.2 Creepage and wear rate

The average COF values of the zone 3 of the curves shown in Figures 6 and 7 were used to build the Carter's curves shown in Figures 8 for dry and lubricated conditions. After 3% of creepage the COF is stabilized in the dry tests. In this case, the slip zone begins to saturate the contact area and the maximum COF is reached. Under these conditions the COF is close to 0.55, which is consistent with the literature [10,14,18] and it is in the interval for dry rail conditions reported by Stock et al [6]. In the lubricated tests (shown in detail in the top left insert in Figure 7), on the other hand, the maximum COF is reached after 5% of creepage and the maximum

value is around 0.07 for both TOR-FM's added.

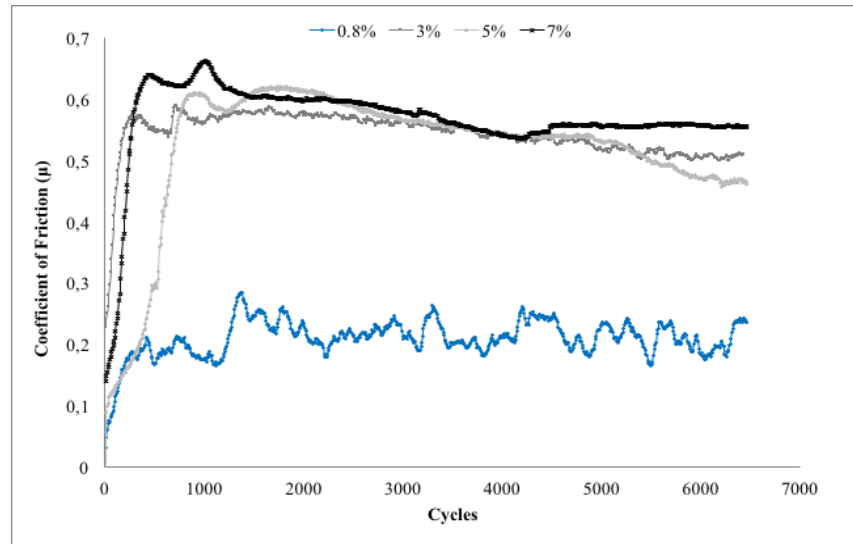


Figure 5. Coefficient of friction under dry conditions.

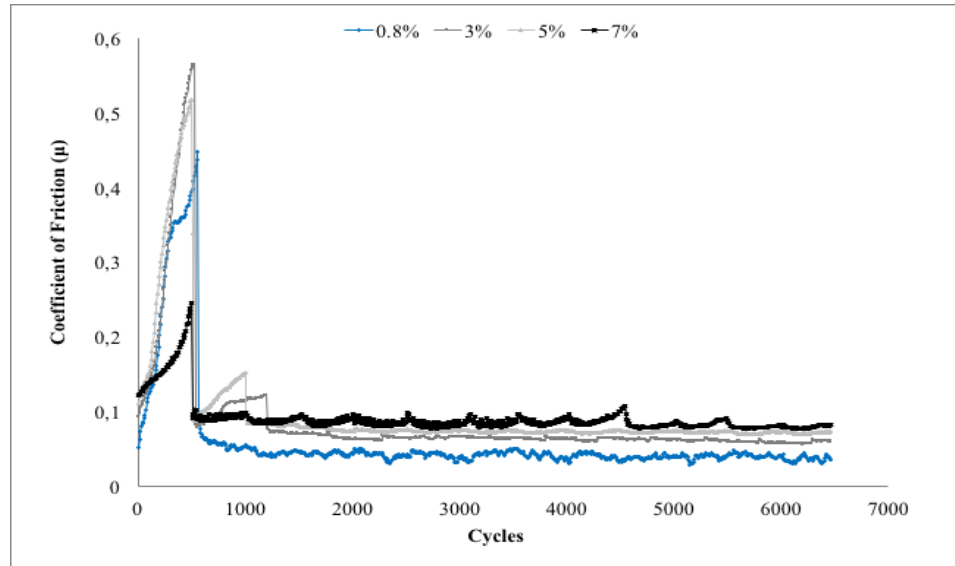


Figure 6. Coefficient of friction for tests with TOR-FM1 and different creepage values.

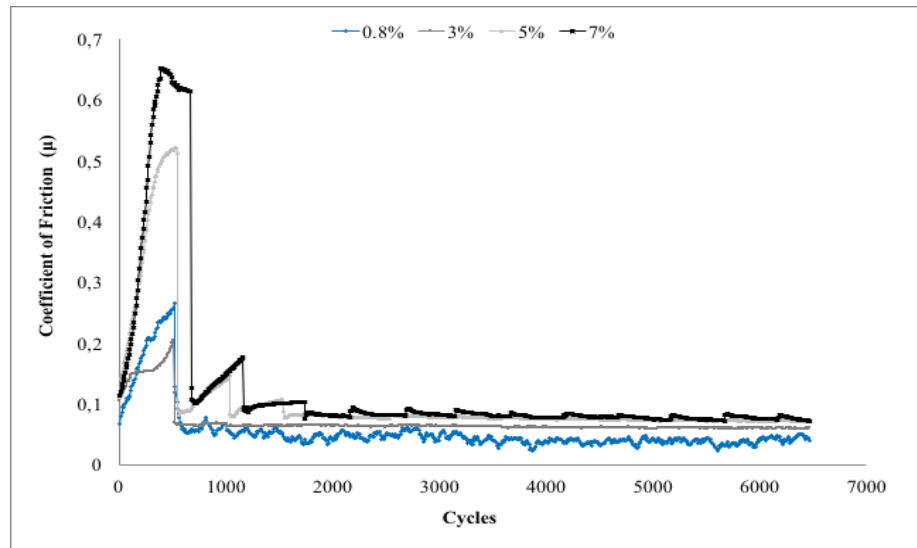


Figure 7. Coefficient of friction for tests with TOR-FM2 and different creepage values.

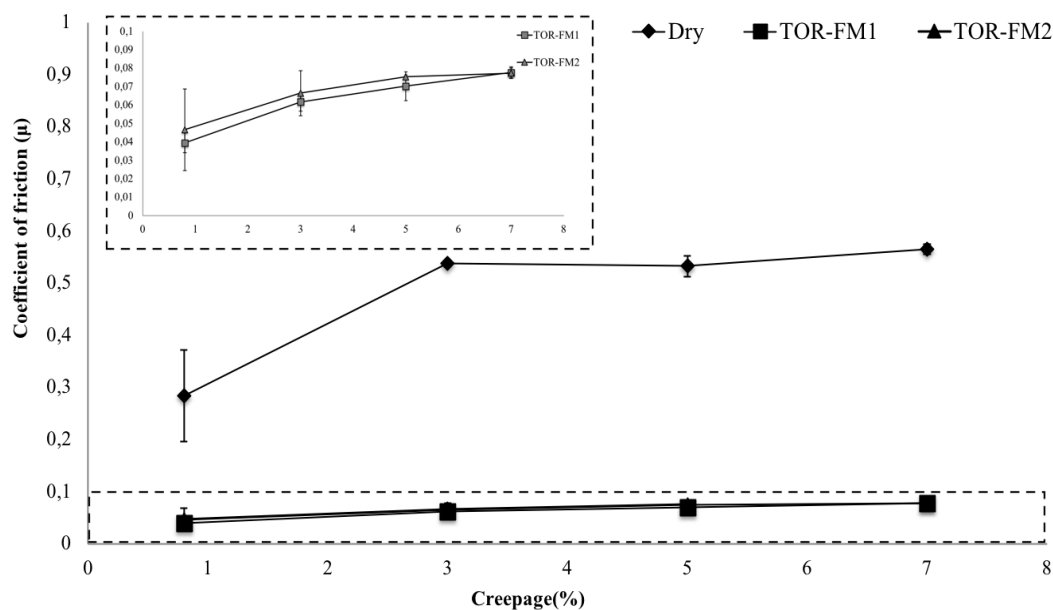


Figure 8. Creep's curves for all test conditions.

Figures 9 and 10 show the measured wear rates for rail and wheel samples as a function of creepage, together with the respective COF variation. For the wheel samples, the dry tests led to higher wear rates compared to the lubricated tests. Both rail and wheel samples tested with TOR-FM2 presented higher wear rate than those tested with TOR-FM1. This result is relevant since the COF is very similar for both TOR-FM's, which indicates that the TOR-FM's can be effective to control friction but not necessarily act the same regarding the type and

intensity of the wear mechanisms responsible for surface damage. Comparing both TOR-FM's, TOR-FM2 has a lower viscosity, so a more intense crack pressurization phenomenon can be expected [19]. This is particularly relevant since during the dry stage in the lubricated tests cracks are formed. When a TOR-FM is added to the contact interface it may enter the cracks and increase its growth rate by hydrodynamic effects. In such case, the delamination process is quicker, and the wear rate is higher.

Generally speaking, the wear rate of the samples is higher when the creepage increases. In the tests with TOR-FM2, however, there is a slight decrease in wear rate when creepage increased from 5% to 7%. This occurs mainly due to an increased oxidation rate because of higher temperatures in the contact area, so the tribological pair experiences a partially-oxidative wear regime. In dry tests with large creepage values a high contact temperature is established as well, but the sub-surface volume affected by significant shear stresses is quite thicker than the oxide layers formed so the oxidative wear regime cannot be established in practice.

The results showed that the rail material has lower wear rates than the wheel material for all the conditions tested. This agrees with the typical behavior described in the literature, even when softer rails are tested [20, 21]. The difference between wear rates for rail and wheel samples is consistent with the fact that in railway systems it is

much easier and cheaper replacing wheels than rails [22].

The wear rates of wheel samples under lubricated conditions were very similar regardless the TOR-FM used, with the sole exception of the tests performed with 0.8% of creepage, in which case the wear rate of wheel samples after the tests with TOR-FM2 were similar to those found in dry conditions. At this point it is worth to remind that the crack pressurization mechanism is not present in the wheel samples in a twin-disc test due to the direction of the stresses in the rolling-sliding contact with respect to the direction of crack opening [11]. Therefore, the high wear rate found in the tests with TOR-FM2 and creepage of 0.8% cannot be attributed to this mechanism. Instead, it may be a consequence of abrasive effects caused by solid-particle additives and/or wide variations in the rheological properties of the TOR-FM. This is a matter of ongoing research and no conclusive evidences can be provided currently.

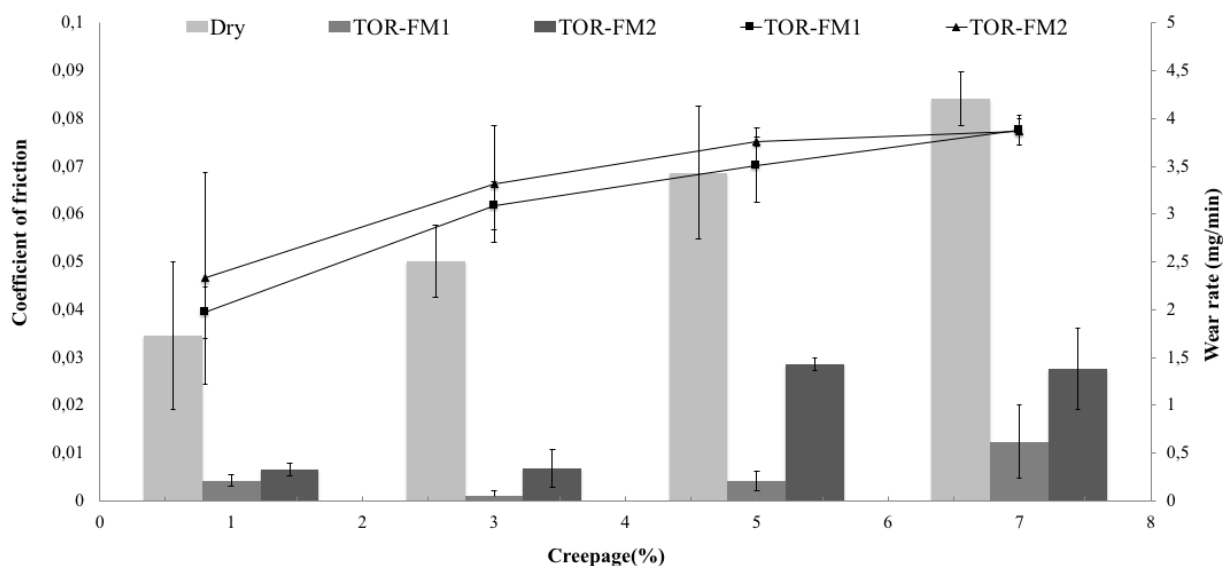


Figure 9. Wear rate of rail samples.

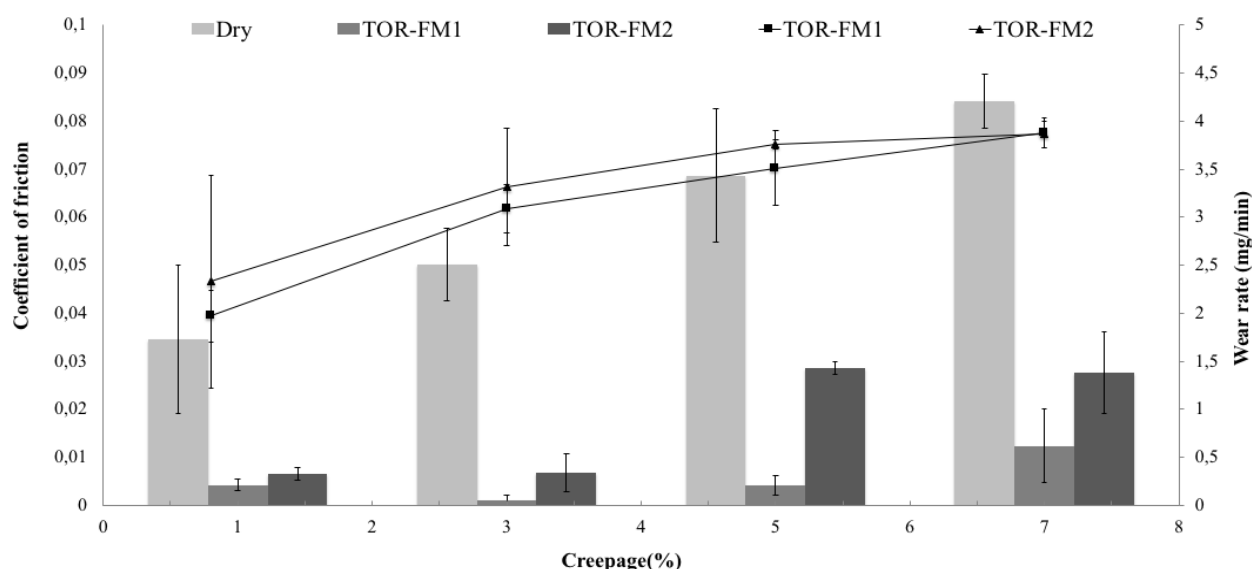


Figure 10. Wear rate of wheel samples.

3.3 Surface Analysis

Figures 11 and 12 show the aspect of the worn surfaces of rail and wheel samples respectively after tests under different lubrication conditions and creepages. Evidences of high plastic deformation in the form of ratcheting marks can be observed. Delamination is more evident for high creepages under lubricated condition (Figures 11b and 12b), which is consistent with the crack pressurization mechanism assisted by the presence of TOR-FM's in the rail samples. For low creepages the shear stresses are low, the surface damage is of less extent and in some cases machining marks can still be observed, which shows that the shear stresses imposed during the tests were of small magnitude. The presence of oxides at the surface is also evident although no homogeneous film seems to be formed.

The surface of the wheel samples shows evidences of low surface damage for the lubricated conditions with creepage of 0.8%, while for higher creepages the plastic deformation is more evident, especially in terms of delamination marks. For the dry tests, adhesion marks can be seen for 0.8% of creepage, being this the main wear mechanism. The variations of roughness parameters did not show a clear trend during the tests, mainly because the aspect of the worn surfaces does not necessarily correlate with the magnitude of the damage. This is explained by

considering that the plastic deformation promotes cyclic processes of delamination and smoothing of the surface, which lead to extensive variations of the values of the roughness parameters depending on which stage (smoothing or delamination) the test is stopped.

3.4 Microstructural Analysis

Figure 13 shows cross-sectional views of the rail samples after the twin-disc tests. It can be seen that creepage has a marked influence on the plastic deformation of the samples. When creepage increases the amount of deformed sub-surface material is greater, reaching hardened depths of around 140 μm approximately under dry conditions. When the top-of-rail friction modifiers were added to the surfaces, the thickness of the deformed material was reduced to circa 50 μm . In dry testing condition the effective shear stress at the surface is much higher and it does have a considerable influence on the size of the deformed volume beneath the contact surface. Also, high tangential forces in the contact promote the crack growth in the sub-surface.

Figure 14 shows cross-sectional views of wheel samples after the tests. As in the case of the rail samples, it is evident that plastic deformation increases with creepage and decreases when a TOR-FM is applied.

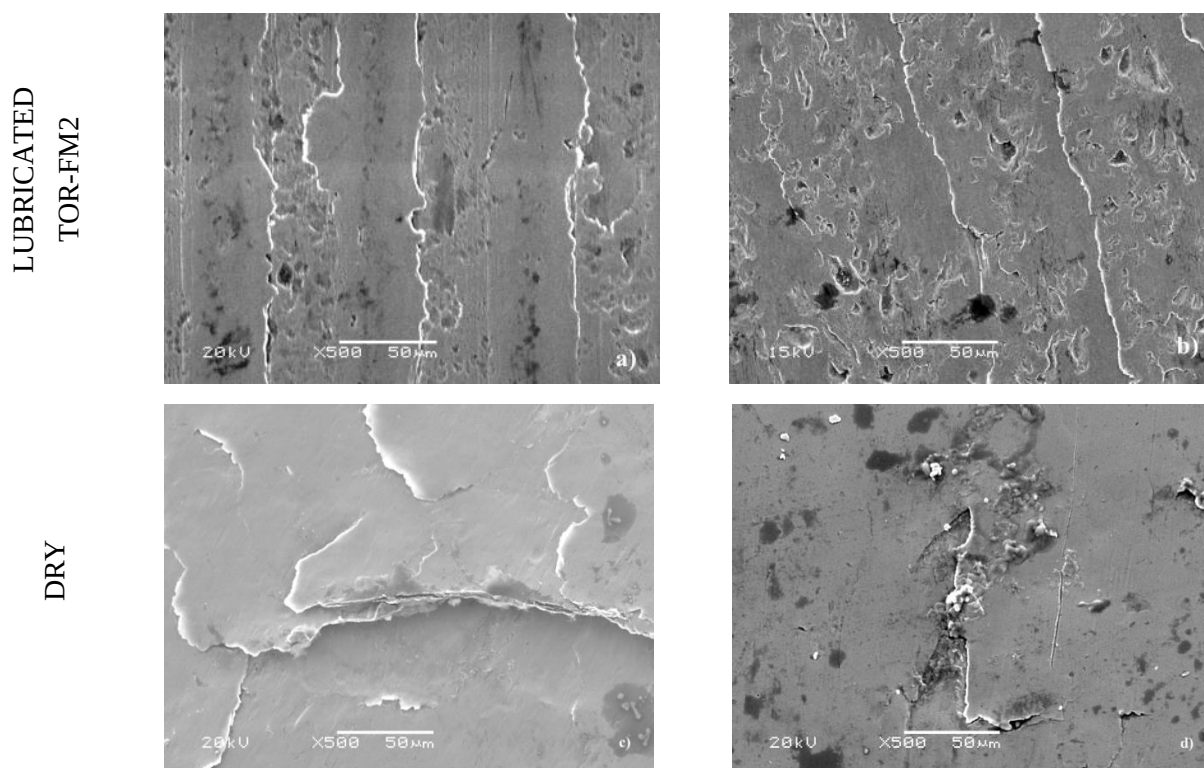


Figure 11. Surface aspect of rail samples after tests with creepage of 0.8% (left column) and 7% (right column). SEM.

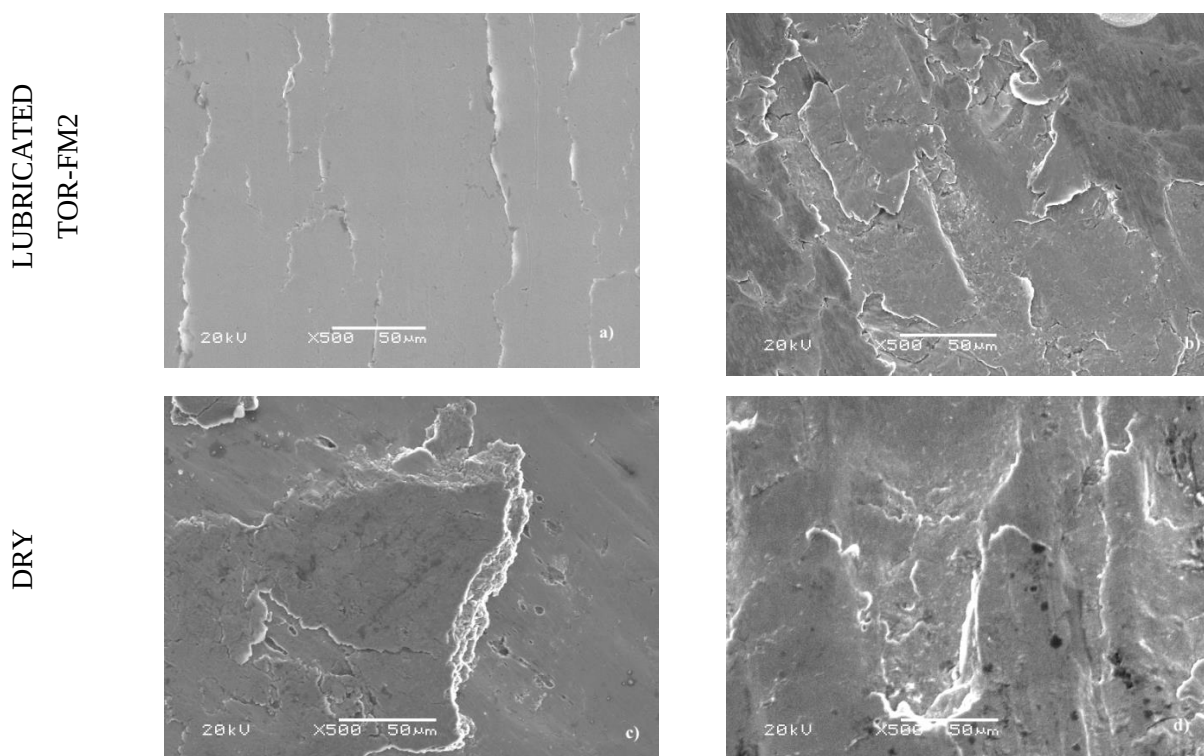


Figure 12. Surface aspect of wheel samples with creepage of 0.8% (left column) and 7% (right column). SEM.

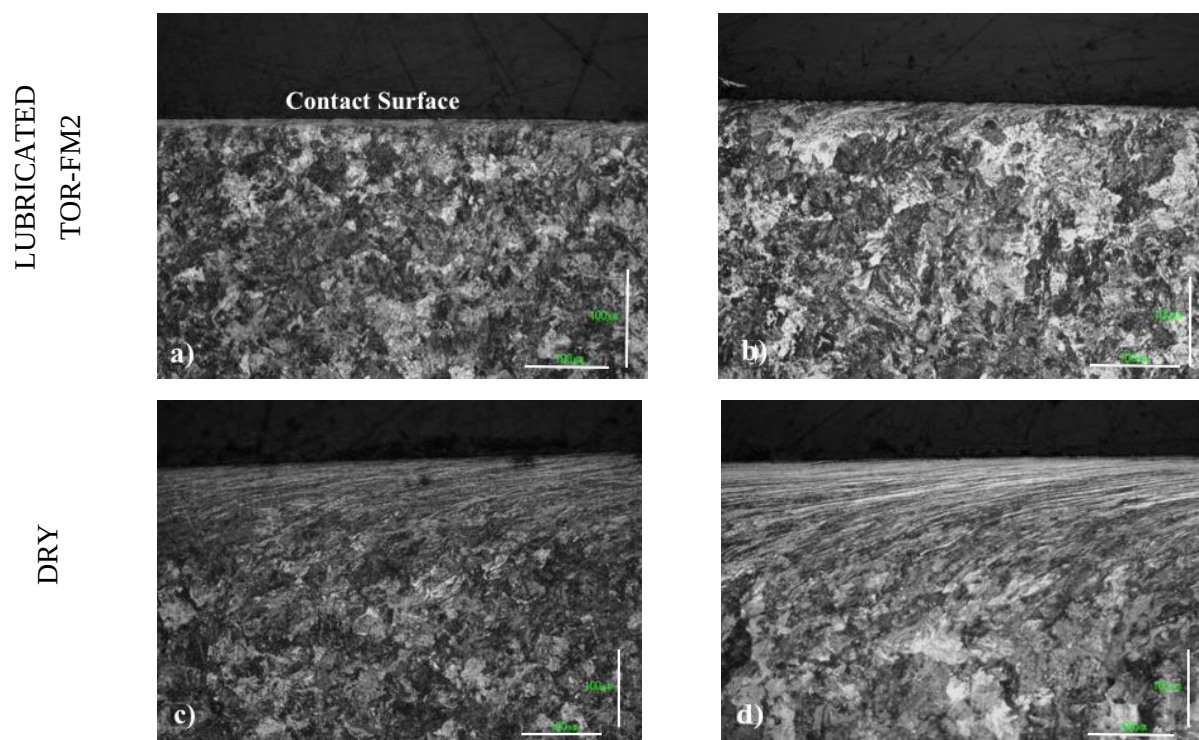


Figure 13. Cross-sectional view of the rail samples after twin-disc tests with creepage of 0.8% (left column) and 7% (right column).

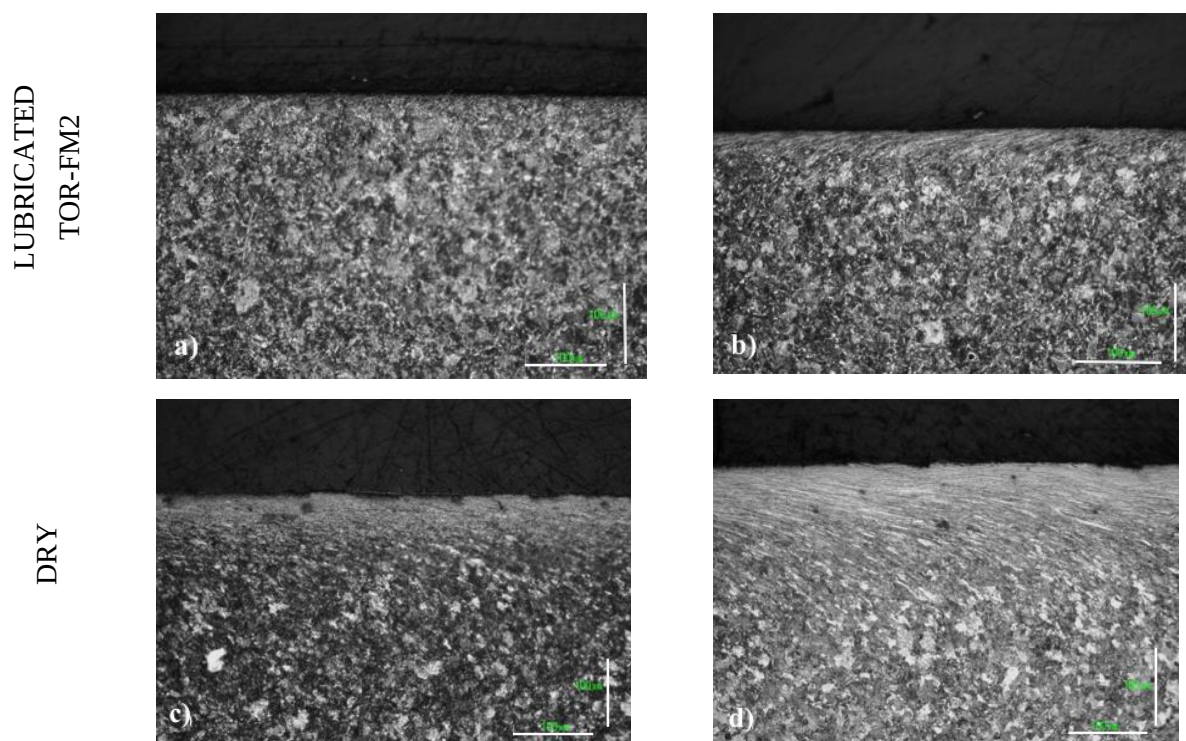


Figure 14. Cross-sectional view of the wheel samples after twin-disc tests with creepage of 0.8% (left) and 7% (right).

Figures 15 and 16 show the micro-hardness profiles of rail and wheel samples for dry (Figure 15) and lubricated (Figure 16) conditions.

Samples tested under dry conditions showed more intense hardening effects due to plastic deformation near the contact surface. The hardening effect was observed up to a depth of 200-300 μm . From this point on the hardness stabilizes around an average value similar to that of the base material. The maximum hardness values at the surface were always higher in rail samples than in wheel samples although no straightforward correlation may be drawn with creepage from the current data set.

For lubricated samples (Figure 16) the micro-hardness profiles do not show significant increases near the contact surface compared to the base material since the TOR-FM reduces the strain hardening effect caused by the traction force at the interface.

Table 3 shows a summary of the maximum values of hardness observed in the samples after the tests and the deformed layer thickness for every testing condition.

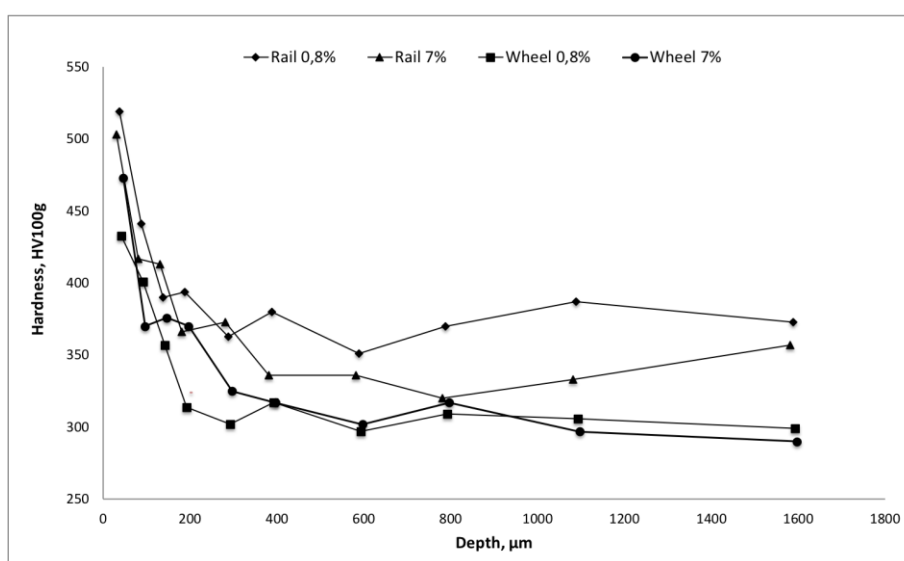


Figure 15. Micro-hardness as a function of the distance from the contact surface. Rail and wheel samples tested under dry conditions.

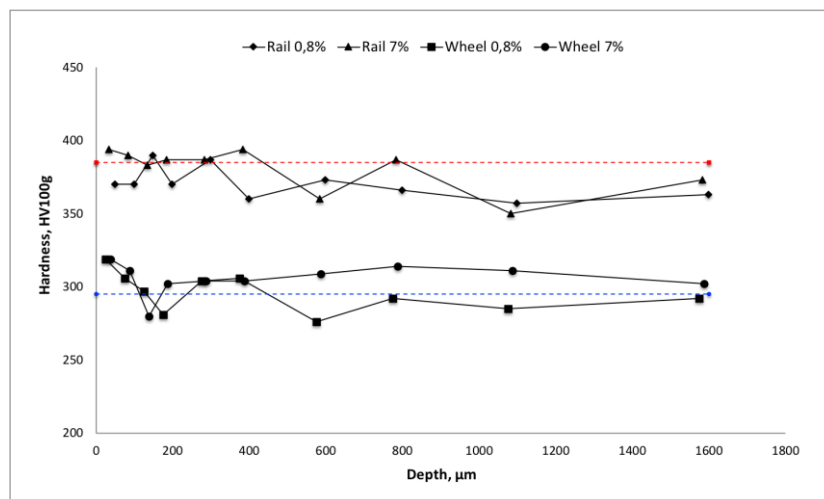


Figure 16. Micro-hardness as a function of the distance from the contact surface. Rail and wheel samples tested under lubricated conditions. The dotted lines show the average hardness of the base material.

Table 3. Maximum hardness reached after each test condition.

	Creepage 0.80%				Creepage 7%			
	Dry		Lubricated		Dry		Lubricated	
	Hardness	Depth	Hardness	Depth	Hardness	Depth	Hardness	Depth
Rail	519 HV	138 μm	390 HV	60 μm	503 HV	110 μm	394 HV	35 μm
Wheel	433HV	192 μm	319 HV	30 μm	473 HV	290 μm	319 HV	38 μm

Generally speaking, the samples tested under dry conditions systematically showed more surface damage and higher wear rate and depth of the plastically deformed region beneath the surface than those tested with the addition of friction modifiers. However, the samples tested with TOR-FM2 presented higher wear rates than those tested with TOR-FM1, which can be related in principle to the effect that the lower viscosity of the former has on the crack-pressurization mechanism: when the FM is added to the contact interface it flows into the surface defects generating a hydrostatic pressure at the tip of the cracks, which leads to a faster crack propagation.

4. CONCLUSIONS

The increase of the creepage in twin-disc tests of R350HT rail samples against ER8 wheel samples led to a significant variation of the COF in dry conditions, with maximum stable COF values between 0.5 and 0.6.

The tests performed with the addition of top of rail friction modifiers (TOR-FM1 and TOR-FM2) yielded stable COF values as low as 0.07, with reduced shear stresses at the contact surface and smaller sub-surface deformed volumes.

The samples tested with the addition of TOR-FM2 showed similar COF values than those measured with the addition of TOR-FM1, but the wear rates were dissimilar, indicating that the wear mechanisms can vary depending on the nature of the friction modified user even for equivalent friction responses.

The plastic deformation represented by ratcheting and delamination is more evident for high creepages under lubricated condition, which can be related with the crack pressurization mechanism in the rail samples in presence of the top of rail friction modifiers, especially in the case of TOR-FM2.

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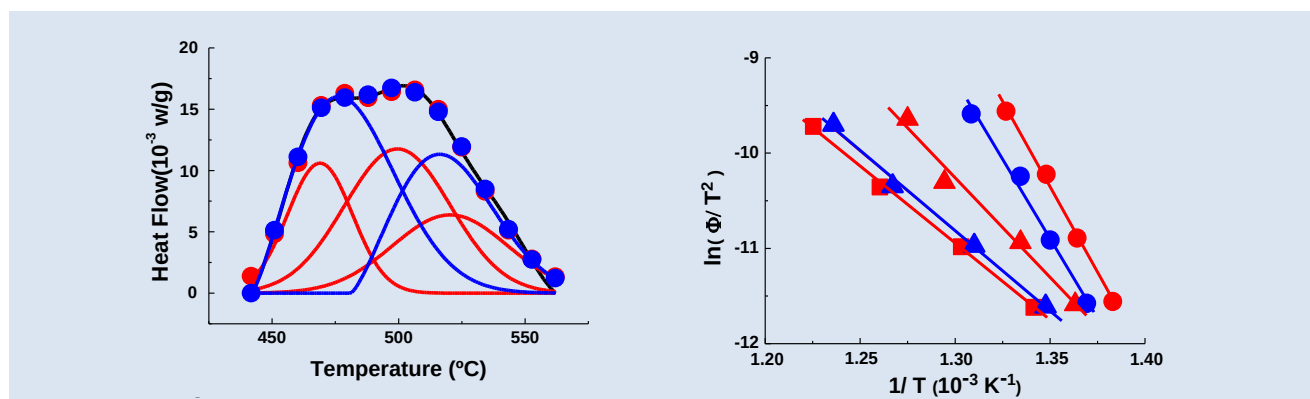
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KINETIC CHARACTERIZATION OF AN AA8011 ALLOY NON-ISOTHERMALLY ANNEALED ABOVE 400°C

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ABSTRACT

Solid state reactions occurring in an Al-Fe-Si alloy are demonstrated through DSC measurements at temperatures above that of recrystallization, where Fe-rich precipitation phases coexist with processes of recrystallized grain growth. These complex reactions are deconvolved for analysis into individual reactions associated to each of the transformation mechanisms involved in the process. Symmetrically distributed Gaussian transfer functions (GTF) and asymmetric Weibull transfer functions (WTF) are used in the deconvolution; and each individual reaction is analyzed through both the Šesták-Berggren (SB) combined kinetic model and the isoconversional scheme, a linear regression determining each of the parameters. The study reflects the drawbacks of kinetic analysis based solely on the fitting of heat flow, as the patent dispersion of kinetic parameters clearly shows. This is corrected by adjusting the activation energy obtained by isoconversion methods. Three reactions are required when using GTF; whereas only two suffice when using WTF. The overall results show that reactions above 400°C occur primarily because of Fe diffusion, and that other reactions occurring in deformed samples have activation energies coinciding with energy diffusion at high-angle grain boundaries.

Keywords: Kinetic Characterization, AA8011 Alloy, Reaction Rate Theory, Non-isothermal annealing.

CARACTERIZACIÓN CINÉTICA DE UNA ALEACIÓN AA8011 RECOCIDA NO-ISOTÉRMICAMENTE POR ENCIMA DE 400°C

RESUMEN

A partir de medidas de DSC se pone en evidencia las reacciones que ocurren en una aleación Al-Fe-Si a temperaturas por encima de la temperatura de recristalización, donde coexisten los procesos de precipitación de fases ricas en Fe y el crecimiento de granos recristalizados. Para su análisis, estas reacciones complejas son deconvolucionadas en reacciones individuales asociadas a cada uno de los mecanismos de transformación involucrados en el proceso. En la deconvolución se utilizan funciones de transferencia simétrica de Gauss (GTF) y asimétrica de Weibull (WTF) y cada reacción individual se analiza a través del modelo cinético combinado de Šesták – Berggren (SB) y el esquema isoconversional; Y mediante regresión lineal se determinan cada uno de los parámetros involucrados. El estudio refleja las falencias del análisis cinético basado solo en el ajuste del flujo de calor, las cuales se manifiestan en una dispersión de valores de los parámetros cinéticos. Este hecho se corrige mediante la fijación de la energía de activación obtenida por el método de isoconversión. La data experimental es cubierta por tres reacciones cuando GTF son utilizadas, mientras que solo dos reacciones son suficientes cuando se usa WTF. Los resultados muestran en general que por encima de 400 °C las reacciones ocurren principalmente por difusión de Fe y que en muestras deformadas ocurren otras reacciones cuya energía de activación coincide con la energía de difusión de contornos de grandes ángulos.

Palabras Claves: Caracterización Cinética, Aleación AA8011, Teoría de velocidad de reacción, recocido no-isotérmico.

1. INTRODUCTION

The microstructural condition achieved by applying thermomechanical treatments on a material, conclusively regulates that material's properties. For example, the aim behind homogenization is, in principle, to create a matrix with few defects and submicroscopic atomic aggregates, so that subsequent annealing allows, with minimum perturbation, the identification of mechanisms generating any transformation in the material, as opposed to rolling, a process that introduces a large number of disturbances, mainly dislocations, in homogenized samples, that directly interact with any other processes, diffusive or otherwise, occurring in the samples. Under these premises it is expected that physical properties, susceptible to structural reordering of atoms and defects in the material, undergo modifications that can be simultaneously generated by more than a single physical mechanism. That is the case of the interaction between recrystallization and phase precipitation in deformed alloys, which is the subject matter of this work. The annealing process covers three major stages: recovery, recrystallization proper, and the growth of recrystallized grains. The first step in this crystal rearrangement is recovery, a process whereby deformed materials are annealed without the high-angle boundary migration [1] occurring below recrystallization temperatures. Both X-ray and electron microscopy have shown that dislocation density significantly decreases during recovery, dislocations tending to arrange themselves into sub-grain cell structures [2]. Haessner [3] has characterized the crystal changes occurring during recovery and recrystallization. Although the frontier between recovery and recrystallization is not well defined, it has been accepted that recrystallization starts with high-angle boundary migration [1]. However, the difference between recrystallization and grain growth lies in the source of the energy from which these processes derive. The energy required for recrystallization stems mainly from dislocation, whereas that for grain growth comes from grain boundaries [4,5], the latter also occurring at higher temperatures [5].

The third step identified in the annealing process is grain growth, which occurs at temperatures above that of recrystallization [5]. Although the recrystallization temperature is conceptually well defined, the fact is that different physicochemical

factors affect its value, such as the microchemistry and composition of the material, the type and magnitude of the deformation [6], the temperature of annealing, the annealing time, and the thermal history of the sample (initial microstructure) [7,8].

This high incidence of the recrystallization process on the mechanical properties of alloys has led to an extensive literature for academic and industrial purposes, as on the one hand, academics and researchers need to understand how different mechanisms capable of magnifying the properties of the material occur and interact; and on the other, there is no end to the ever-expanding interest for lightweight, ductile and resistant materials with an optimal cost-investment ratio.

This effort has resulted in the implementation of thermo-mechanical treatments that enhance the refinement of the recrystallized grain [9,10], and are able to control or inhibit the formation of textures [7,11,12] that affect the formability of the material [13,14,15]. Furthermore, novel experimental techniques and theoretical studies have been incorporated [16-19] that lead to a better characterization of all the reactions taking place during annealing, which makes it possible to ascertain precisely when the restoration of the crystal has occurred. The softening of the deformed material after annealing, detected through yield stress variation, is revealed as one of the most effective methods to discern the evolution of recrystallization during annealing [7].

Furthermore, some authors have reported different behaviors during isothermal and non-isothermal annealing [20], basically because of the different ways in which both treatments modify the factors affecting each of the annealing stages. Sepehrban et al. [21] have studied the interaction of precipitation at each stage of non-isothermal annealing in an Al-Mg-Si-Cu alloy; and report different behaviors according to the heating rate. A similar effect is reported by Khani Moghanaki et al. [22] in a severely deformed 2024 aluminum alloy.

This work complements the experimental and theoretical studies carried out by the author and collaborators [23-25] on the effect of deformation on AA8011 alloys subjected to both isothermal and non-isothermal annealing. The use of DSC, thermoelectric power and its derivative highlights the existence of two transformations in the homogenized samples, one associated with precipitation of α -

AlFeSi at temperatures below 400°C, and another with β -Al₃Fe near 470°C. Rolling accelerates the precipitation of the α phase up to a defined degree of deformation, suggestive of both reorganization of the dislocation structure and interaction between recrystallization and precipitation. Simultaneous interactions are established between precipitation of Guinier-Preston zones and other Si-rich aggregates and crystal recovery at temperatures below 150°C; and between α -AlFeSi phase precipitation and recrystallization in the 200 - 400°C temperature range.

Above 400°C the β phase is less affected by the rolling process; and both DSC and the thermoelectric power derivative place the temperature at the start of β precipitation in the neighborhood of 400 °C, coinciding with that at the final stage of recrystallization and growth of recrystallized grains. Pre-aging at different temperatures shows that recrystallization starts at 300°C. Transmission Electron Microscopy (TEM) shows the presence of recrystallized grains at both 475°C and 502°C. These results beg the conclusion that, above 400°C, completion of recrystallization and grain growth in AA8011 alloys occurs simultaneously with Fe-rich phase precipitation.

Cordovilla et al. [26] by DSC, and Luiggi [27] by both DSC and thermoelectric power, report phase precipitation reactions above 400°C in AA8011, that undoubtedly involve Fe and Si diffusion. For both authors, recrystallization is strongly affected by the heating rate during non-isothermal annealing, this transfer occurring at a higher temperature when the heating rate is higher. These authors locate the recrystallization peak at 380°C at heating rates of 40°C/min [26], while Roy et al. [28] locate it at 352°C for heating rates of 10°C/min.

A diagram produced by Shoji et al. [29] reports both α -AlFeSi phase precipitation in a 70% cold-rolled AA1200 alloy occurring at temperatures of up to 400°C and the presence of Al₃Fe precipitates above that temperature. Raghavan [30], for his part, in his evaluation of the phase diagram of an Al-Fe-Si, identified up to seven compounds of different stoichiometry that may result as a consequence of the Fe/Si concentration ratio in the alloy; whereas Vybornov et al. [31] identified the presence of stable β -AlFeSi precipitates at 550°C. Other authors [32-34] have observed θ -Al₃Fe, α -AlFeSi, and β -AlFeSi phases reported as equilibrium phases. Kumar et al.

[35] recently performed a deformation and recrystallization study on the microstructure and texture development of an AA8011 alloy, and found out that the annealing parameter combination to yield optimal texture deformation and recrystallization for improving this alloy's formability was 375°C and 4 hours.

Luiggi [26] has confirmed that it is difficult to obtain pure reactions in multicomponent alloys, whereby a sole mechanism might account for the transformation measured. He also asserts that the kinetic analysis of the overall reaction is not always representative of the individual reactions that might occur. Hence, for a detailed analysis of the mechanisms involving the microstructural changes brought forth in the alloy, a mathematical procedure known as signal deconvolution [36-41] is used to separate the overall transformation in individual reactions. This paper endeavors, therefore, to determine the kinetic parameters associated to each individual transformation deconvolved from the overall reaction measured by DSC in AA8011 samples at temperatures above 400°C, where phase precipitation and grain growth process coexist.

The paper has been organized as follows: Section II introduces the theory of reaction kinetics and the isoconversion model, as well as the related deconvolution aspects. Section III elaborates on the experimental outlook; and Section IV parses the results and discussion.

2. THEORETICAL ASPECTS

2.1 On the kinetic theory

The theory necessary to carry out the present investigation totally corresponds with the one explained by Luiggi and Valera in this same journal [42], reason why the supporting equations have been obviated, and the reader is invited to review said reference.

We first consider the theory of reaction, where the reaction rate is defined by the time evolution of the extent of conversion α . Both the isothermal and the non-isothermal evolution of α follow the same equation, and the conversion from one to the other is achieved by introducing the heating ratio $\beta = dT / dt$. The reaction rate, in its simplest form, involves a reaction constant $K(T)$, which in principle follows an Arrhenius relation (It is not always so [43]), and a kinetic function $F(\alpha)$ associated with the reaction's

generating mechanism. Similarly, this reaction rate can be determined directly from the measurements of heat flow duly weighed by the enthalpy of the reaction.

This approach relates the parameters defined in both $K(T)$ and $F(\alpha)$ with the heat flow measurements obtained by DSC. The parameters of $K(T)$ are the prefactor A and the activation energy Q , while the kinetic function selected is the truncated Šesták - Berggren [44,45], whose parameters are n and m . The kinetic analysis is, therefore, reduced to obtaining parameters A , Q , m , and n that reproduce the experimental data.

2.2 Evaluation of kinetic parameters

Considering the rate reaction equation, and explicitly including the expressions of $K(T)$ and the Šesták-Berggren two-parameter kinetic function $F(\alpha)$ [44,45], the following equation is obtained (see appendix A),

$$\ln\left(\frac{\Delta H_{\alpha}}{S(1-\alpha)^n \alpha^m}\right) = \ln(A) - \frac{Q}{RT} \quad (1)$$

where $\Delta H_{\alpha} = \int_0^{\alpha} \Delta H d\alpha$ represents the area under the heat flow curve ΔH from the start of the reaction until a time $t\alpha$ has elapsed. The best m and n values linearizing Equation (1) were obtained by linear regression with an $R^2(L)$ determination factor closer to 1. The conversion extent α was limited to the range between 0.05 and 0.95, a range larger than that of our previous study [42], basically to take advantage of the best tail effect that Weibull functions grant to fittings of experimental data. At this stage it is worth wondering whether a relation of uniqueness exists between parameters n and m in Equation (1) and the value $-Q/R$ guaranteeing that equation's linearity. The answer is negative since different sets of parameters might well adjust the experimental data in such a way that Equation (1) is a straight line; however, the ambiguity over parameters can be reduced by directly deriving the activation energy by isoconversion [25].

As for activation energy, there is such an implicit dependence of ΔH on β that its value is mainly regulated by the natural logarithm of the quotient between the experimental data and the kinetic function adjusted for these data. The literature shows that for processes involving crystallization, there

exists a decreasing dependence on Q when β increases [46]; however, there seems to be no reference in the literature for processes involving the coexistence of several processes, making it impossible to obtain an activation energy independent from experimental data, sample geometry, and heating rate [47].

2.3 The Isoconversion Method

The isoconversion method is based on the fact that for the same conversion extent α , the functions depending on α will remain constant. For example in Equation (1) there will be a ΔH curve for each heating ratio β , and therefore, the function $F(\alpha)$ in the denominator of that relation will remain constant for a fixed value of α in each of the β considered. This implies that in order to have access to the activation energy, explicit knowledge of the kinetic function is not required in advance. In this work, the activation energy is evaluated using the isoconversion relation referenced in [48], the temperature peaks for different values of β being identified from the deconvolved curves,

$$\ln\left(\frac{\beta}{T^N}\right) = \ln(A) - \frac{Q}{RT} \quad (2)$$

where T represents the peak temperature of the deconvolved reaction; and β , the respective heating rate. This relation allows for the graphic determination of Q and A values for a known value of N . The dispersion of the Q values inferred for the same microstructural condition and different β from the previous section does not allow a single reference value of Q to determine the best value of N and the other kinetic parameters. Hence, $N=2$, which is equivalent to using Kissinger's relation [49]. Resorting to other N values, in harmony with other models in the literature, generates Q values not very different from those obtained via the Kissinger method. Since isoconversion methods get their true meaning when the kinetic triplet is specified, to wit: Q , A , and $F(\alpha)$ [50], certain approximations are frequently used to finally assess the additional parameters appearing in the different kinetic functions; e.g., the N evaluation in the JMAEK scheme [51].

The methodology followed in this work purports to ascertain Q from Kissinger plots and then use Equation (1) to obtain, from Šesták-Berggren, n and

m values that linearize that equation in an energy range defined by $Q \pm 0.005 Q$.

2.4 Deconvolution of experimental curves

The analysis of overall signals in multiple response systems tends to arrive at conclusions masking actual individual results. Such is the case of differential thermal analysis in multicomponent alloys where the signal measured covers a number of particular effects only separable by mathematical deconvolution techniques.

Deconvolution is a highly important tool in the treatment of signal processing based on the principle of linearity and time invariance of the signal. The convolution integral defines the output signal $Y(t)$ generated by one or several input impulses $X(t)$ owing to a transfer function $g(t)$ [52,53]:

$$Y(t) = X(t) * g(t) = \int_{-\infty}^{\infty} X(\tau)g(t - \tau)d\tau \quad (3)$$

The opposite of convolution is deconvolution, whereby knowing the output $Y(t)$ and the transfer function $g(t)$, it is possible to determine the attainable input functions generating said output [54]. In this study, the output signal is the heat flow measured by DSC. The wide array of transfer functions available can determine particular input signals.

Deconvolution in this paper is performed by means of PeakFit (Systat Software Inc.), whose great versatility in signal separation and analysis, and its spectroscopy, chromatography, statistics and miscellaneous sections, allow for conclusive results of a wide variety of peaks. Two types of transfer functions were selected for this analysis.

1. Gaussian Function [55]:

$$W = W_0 \exp \left[-\frac{1}{2} \left(\frac{T - W_1}{W_2} \right)^2 \right] \quad (4)$$

where W represents heat flow; T , the temperature; and W_0 , W_1 , and W_2 represent the amplitude, center and width of the curve, respectively.

2. Weibull Function [56]:

$$W = W_0 \left(\frac{W_3 - 1}{W_3} \right)^{\frac{1 - W_3}{W_3}} \left(\frac{T - W_1}{W_2} + \left(\frac{W_3 - 1}{W_3} \right)^{\frac{1}{W_3}} \right)^{W_3 - 1} \exp \left[- \left(\frac{T - W_1}{W_2} + \left(\frac{W_3 - 1}{W_3} \right)^{\frac{1}{W_3}} \right)^{W_3} + \frac{W_3 - 1}{W_3} \right] \quad (5)$$

which includes a fourth parameter, W_3 , that regulates the form or asymmetry of the peak.

3. EXPERIMENTAL

3.1 Samples studied

An Al-Fe-Si alloy, commercially known as AA8011, was selected, supplied in as-cast form by C.V.G. ALCASA Venezuela, after a process of twin-rolling, cast in 6-mm strips, and then milled to 0.5 mm. It is from samples with this latter thickness that the homogenization and rolling treatments of the present study are initiated. Its composition is provided in Table 1.

Table 1. Chemical composition of alloy AA8011 (wt%).

Al	Fe	Si	Mn	Zn	Cr	Cu
Rem	0.56	0.40	0.01	0.004	0.003	0.01

3.2 DSC equipment and thermal treatment

Heat flow was measured with a Netsch STA-Jupiter 499 calorimeter, whose sensitivity allowed detection of very small heat flow fluctuations.

Three initial microstructural conditions were considered: 1. Samples homogenized during four hours at 600°C, then quenched in water at 2°C (HS); 2. HS samples cold rolled down to 50% gauge in a two-high rolling mill, hence the designation 50-DHS; and 3. Samples similar to those of condition No. 2 but having undergone an 85% thickness reduction, designated as 85-DHS.

To evidence the reactions occurring above 400°C, in particular Fe-rich phase precipitation and grain growth, samples were heated between room temperature and 600°C, the temperature range above 400°C being selected for each of the samples considered.

4. RESULTS AND DISCUSSION

4.1 Heat flow measurements

Figure 1 displays heat flow variation versus temperature for the AA8011 alloy in HS samples heated at different rates.

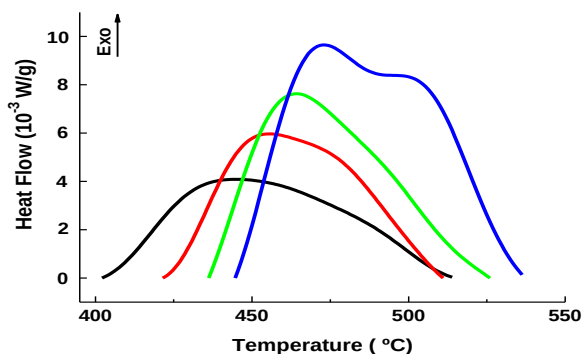


Figure 1. Heat flow versus temperature for HS samples of an AA8011 alloy at different heating rates (β). Black: $5^{\circ}\text{Cmin}^{-1}$. Red: $10^{\circ}\text{Cmin}^{-1}$. Green: $20^{\circ}\text{Cmin}^{-1}$. Blue: $40^{\circ}\text{Cmin}^{-1}$.

The figure shows the complex diffusive-like reaction that seems to be a consequence of at least two physical mechanisms, evident at the $40^{\circ}\text{Cmin}^{-1}$ curve. Fe-rich phase precipitation has been reported for this microstructural condition at that temperature range, especially that of Al_3Fe and Al-Fe-Si of variable composition [30,31]. Heat flow, and particularly the peak of the reaction, increases as the heating rate increases, heralding larger enthalpy reactions.

Figure 2 shows the heat flow variation versus temperature for 50-DHS samples of an AA8011 alloy at different heating rates.

The behavior shown in this figure seems less complex than that of HS samples, although the difference in kinetics indicates the existence of one or several different reactions with respect to the previous one. The rolling effect seems to generate a microstructural rearrangement. In addition to the phases already indicated for the homogenized samples, high-angle boundary migration and the development of recrystallized grains are expected [4]. As in the previous case the reaction peak is higher for larger β . This result implies that a moderate rolling process favors the precipitation of phases once the recovery and recrystallization processes

have taken place, since the tangle of defects and dislocations capable of anchoring the atomic movement has disappeared.

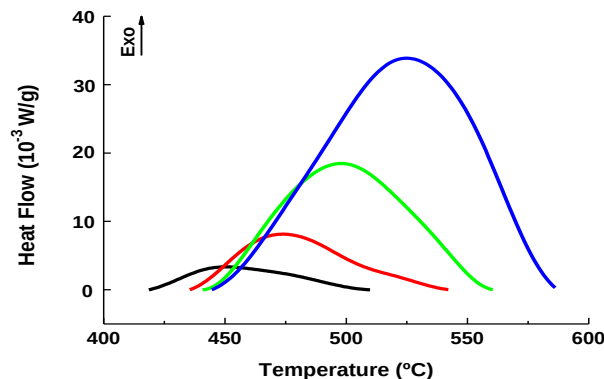


Figure 2. Heat flow versus temperature for 50-DHS samples of an AA8011 alloy at different heating rates (β). Black: $5^{\circ}\text{Cmin}^{-1}$. Red: $10^{\circ}\text{Cmin}^{-1}$. Green: $20^{\circ}\text{Cmin}^{-1}$. Blue: $40^{\circ}\text{Cmin}^{-1}$.

Figure 3 plots heat flow versus temperature of an AA8011 alloy for 85-DHS samples heated at different heating rates. A complex behavior is reflected here, different from the prior one due to the larger number of defects and irregularities introduced in this type of sample.

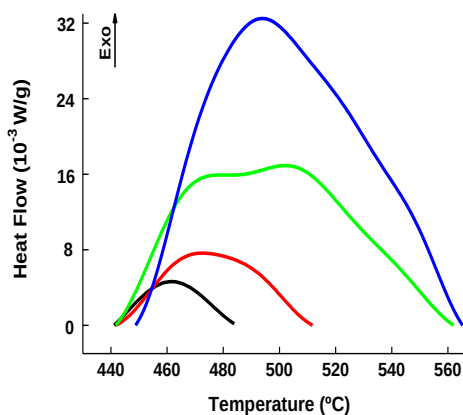


Figure 3. Heat flow versus temperature for 85-DHS samples of an AA8011 alloy at different heating rates (β). Black: $5^{\circ}\text{Cmin}^{-1}$. Red: $10^{\circ}\text{Cmin}^{-1}$. Green: $20^{\circ}\text{Cmin}^{-1}$. Blue: $40^{\circ}\text{Cmin}^{-1}$.

4.2 Deconvolution of heat flow curves

Experimental kinetics are first deconvolved using Gaussian and Weibull transfer functions, both defined in Section 2.4. The validity criterion to fit theoretical and experimental data is set through the determination regression coefficient $R^2(D)$, a

minimum value of 0.99 being required for this adjustment to be considered valid. The number of reactions during deconvolution is set by this criterion. The kinetics deconvolution for the three microstructures under study required, in each case, three reactions when Gaussian transfer functions were used, and two when using Weibull. This difference in the number of reactions might cast doubts on the efficacy of the method to determine the mechanisms generating the kinetics; it is, however, a consequence of the symmetry of the Gaussian function and the asymmetry of Weibull functions.

4.2.1 Kinetic deconvolutions in HS samples

Figure 4 displays heat flow variation versus temperature, as a result of the experimental data's deconvolution measured at different heating rates in homogenized AA8011 samples using Gaussian transfer function.

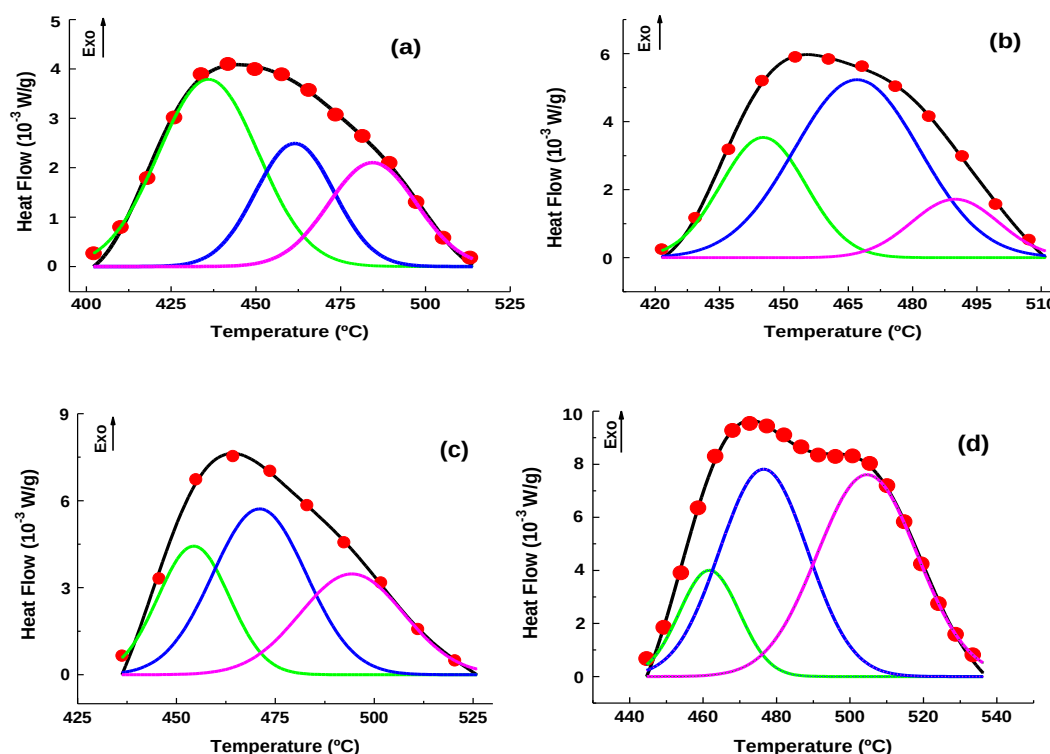


Figure 4. Deconvolution plots using Gaussian transfer function showing heat flow vs temperature for HS samples for different heating rates. a. 5 °Cmin⁻¹ b. 10 °Cmin⁻¹ c. 20 °Cmin⁻¹ d. 40 °Cmin⁻¹.

Both the experimental and theoretical curves are highlighted in each of these figures, in addition to the different reactions obtained by deconvolution. In principle, for this microstructural condition, precipitates of differing Fe/Si ratios, and stable Al₃Fe phase precipitates are expected to coexist. The possibility of co-existence of these reactions is enhanced by Langsrud [57], where intermetallics with different structures can be formed depending on the Fe/Si ratio in Al-Fe-Si alloys. Each deconvoluted

reaction can be characterized by both the position of its peak and its enthalpy, although there is no way to identify any of them, despite the fact that the first one in Figure 4.a; the second, in Figures 4.b and 4.c; and the third, in Figure 4.d, show areas larger than those of the others.

These reactions confirm that phase precipitation in multicomponent commercial alloys does not occur by means of a unique reaction, even though the DSC curves show a single peak.

The same experimental data are analyzed using Weibull transfer functions. This analysis is presented in Figure 5. Due to the asymmetry of this transfer function, only two reactions are needed to meet the

condition $R^2 > 0.99$.

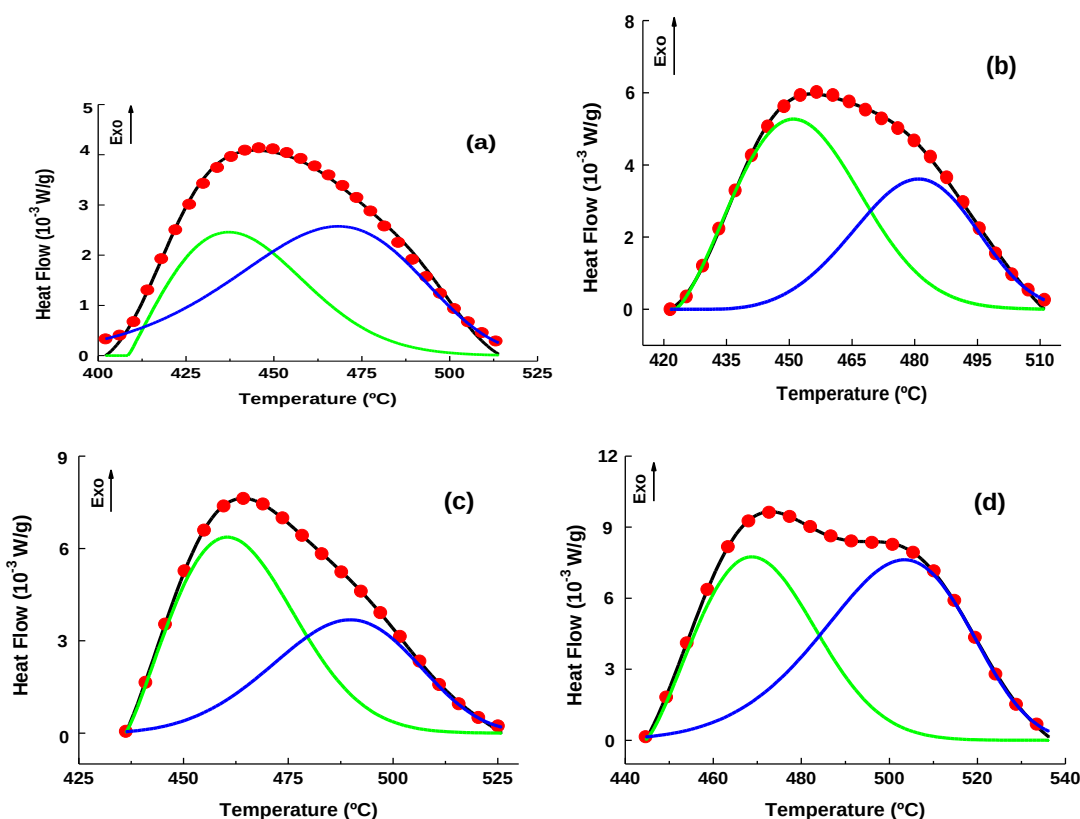


Figure 5. Deconvolution plots using Weibull transfer function, showing heat flow vs temperature for HS samples for different heating rates. a. 5 °Cmin⁻¹ b. 10 °Cmin⁻¹ c. 20 °Cmin⁻¹ d. 40 °Cmin⁻¹.

Deconvolved reactions are not so different in area, a condition that poses competitiveness between the two precipitation mechanisms generating the experimental kinetic. The diffusive character of the mechanisms controlling the reactions and moving the peaks towards the high temperatures when the heating rate is greater is a confirmation of the coexistence of both reactions, as shown in particular by Figure 5.d.

Table 2 displays W_i deconvolution parameters for HS samples. It also includes the total transformation area (Stotal: Total area under the reaction curve) and the area for each particular reaction. Stotal increases

as heating ratio β increases, the particular areas not following the same pattern. A similar disposition can be observed in W_1 , corresponding to the temperature of maximum transformation in °C, each reaction reaching higher temperatures as β increases, confirming that each of these particular reactions hinges on a diffusive mechanism. As for the value of R^2 , a better overall reproduction of the experimental data can be attained when Weibull functions are used, owing to W_3 reflecting in all cases the asymmetry of both reactions, and reproducing more effectively the start and endpoints of the experimental curve.

Table 2. Deconvolution parameters for Gaussian and Weibull transfer functions for AA8011 HS samples.

β °C min ⁻¹	S _{Total}	R ² TF	Reaction	W ₀	W ₁	W ₂	W ₃	S
5	0.28029	0.9968 G	1	0.0037906	436.000	14.713		0.1398
			2	0.0024932	461.486	11.562		0.0722
			3	0.0021034	484.419	12.941		0.0682
10	0.32388	0.9984 G	1	0.0035368	445.181	9.9228		0.0879
			2	0.0052311	467.027	14.6608		0.1922
			3	0.0017200	489.894	10.1282		0.0437
20	0.38410	0.9975 G	1	0.0044363	453.366	8.99940		0.1000
			2	0.0057198	471.009	11.8355		0.1698
			3	0.0034773	494.361	13.1239		0.1144
40	0.57662	0.9977 G	1	0.0040091	461.729	8.13644		0.0818
			2	0.0078178	576.483	12.0109		0.2354
			3	0.0076098	504.685	13.6032		0.2595
5	0.28512	0.9948 W	1	0.0024598	437.141	39.6436	2.0433	0.1121
			2	0.0025749	468.323	197.766	7.9333	0.1730
10	0.32214	0.9989 W	1	0.0052717	451.022	35.4609	2.4040	0.1909
			2	0.0036096	480.933	56.9331	4.0920	0.1312
20	0.38135	0.9998 W	1	0.2229891	460.422	32.0313	2.1964	0.2230
			2	0.1583588	489.789	74.324	4.5808	0.1584
40	0.57288	0.9997 W	1	0.2508606	468.758	30.8704	2.3229	0.2509
			2	0.3220156	503.422	104.750	6.6623	0.3220

4.2.2 Kinetic deconvolutions in 50-DHS samples

Figure 6 displays the kinetic deconvolutions in 50-DHS samples using Gauss transfer functions. Under this microstructural condition at that temperature range, the precipitation occurring in HS samples and a process associated to recrystallized grain boundary migration must ensue.

Furthermore, owing to different factors modifying recrystallization some remnants of this precipitation process should be considered. Although three Gaussian functions are needed for the experimental data reproduction, in each case one or two reactions would prevail, which can be associated to the precipitation process, whereas the remaining lesser-enthalpy reaction might be related to high-angle grain boundary migration or grain growth.

Figure 7 shows the kinetic deconvolution in 50-DHS

samples using Weibull transfer functions. Two deconvolved reactions are shown. This behavior is the comportment expected for a homogenized, quenched, and 50% cold-rolled microstructure, where a strong reaction associated with the precipitation of an iron-rich phase is simultaneously manifested with a reaction of much lesser enthalpy associated to grain growth. Moderate rolling seems to have a double effect on kinetics, the first one generating an atomic arrangement with a propensity to favor only one kind of precipitates; and the second, inducing a simultaneous reaction associated to grain growth, the enthalpy in this second reaction augmenting as β increases. This result seems ideal to analyze the interaction between phase precipitation and recrystallized grain growth.

Table 3 shows deconvolution parameters obtained for kinetics in 50-DHS samples. The increase of S_{total}

with a β increase is again reported, as well as the diffusive character of the individual reactions. Deformation, with respect to HS samples, increases the overall area under the transformation (except for $5^{\circ}\text{Cmin}^{-1}$), a phenomenon suggestive of another

mechanism or other mechanisms taking place for samples with this microstructural condition. The asymmetry of the precipitation reaction changes little with β increase; unlike that of the second reaction, which grows significantly as β increases.

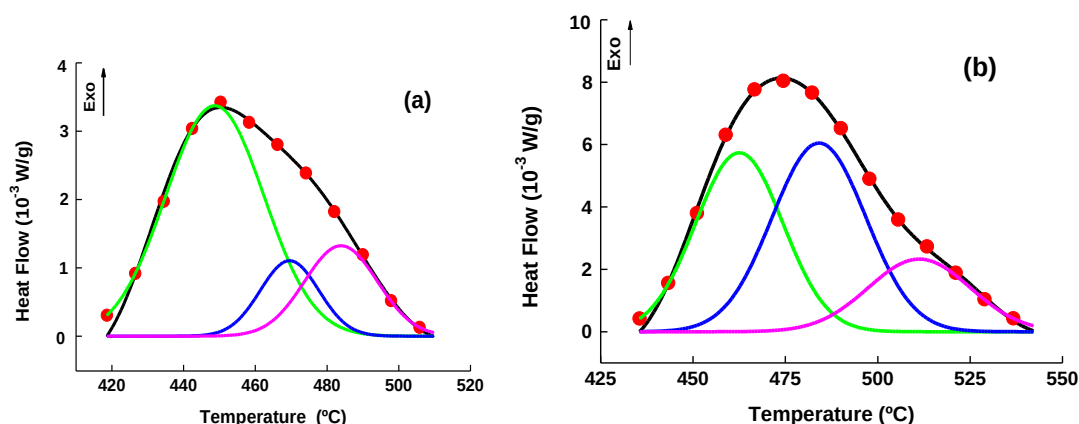


Figure 6. Deconvolution plots using Gaussian transfer function and showing heat flow vs temperature for 50-DHS samples for different heating rates. a. $5^{\circ}\text{Cmin}^{-1}$ b. $10^{\circ}\text{Cmin}^{-1}$ c. $20^{\circ}\text{Cmin}^{-1}$ d. $40^{\circ}\text{Cmin}^{-1}$.

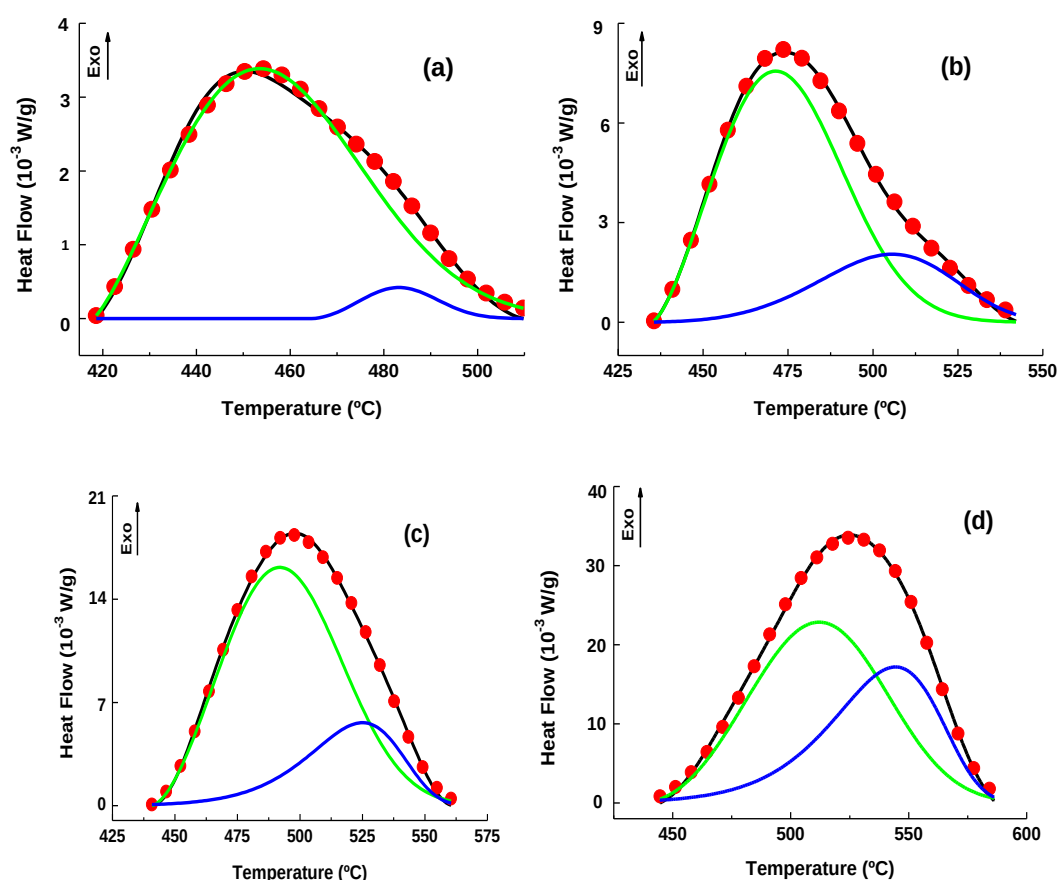


Figure 7. Deconvolution plots using Weibull transfer functions, showing heat flow vs temperature for 50-DHS samples for

different heating rates. a. 5 °Cmin⁻¹ b. 10 °Cmin⁻¹ c. 20 °Cmin⁻¹ d. 40 °Cmin⁻¹.

Table 3. Deconvolution parameters for Gaussian and Weibull transfer functions for AA8011 50-DHS samples.

β °C min ⁻¹	S _{Total}	R ² TF	Reaction	W ₀	W ₁	W ₂	W ₃	S
5	0.17251	0.9955 G	1	0.0033738	448.701	13.743		0.1162
			2	0.0011042	469.551	8.1679		0.0226
			3	0.0013243	483.889	10.144		0.0337
10	0.44299	0.9986 G	1	0.0057416	462.520	11.809		0.1699
			2	0.0060486	484.105	12.697		0.1925
			3	0.0023289	511.241	13.795		0.0805
20	1.20577	0.9990 G	1	0.0061853	471.227	12.276		0.1903
			2	0.0179419	499.744	18.718		0.8418
			3	0.0055669	531.297	12.442		0.1736
40	2.63450	0.9992 G	1	0.0097836	482.661	16.553		0.4059
			2	0.0321446	521.404	21.890		1.7638
			3	0.0127612	553.430	14.530		0.4648
5	0.17187	0.9952 W	1	0.0033864	453.446	45.6784	2.2950	0.1637
			2	0.0004303	483.315	21.9301	2.8486	0.0082
10	0.44083	0.9990 W	1	0.0075606	471.362	44.9460	2.4803	0.3386
			2	0.0020494	505.724	90.0385	4.7940	0.1022
20	1.20455	0.9990 W	1	0.0161558	491.938	61.3540	2.6655	0.9319
			2	0.0056271	525.019	311.876	17.468	0.2726
40	2.63627	0.9989 W	1	0.0228547	512.057	86.6841	3.1701	1.6063
			2	0.0171915	544.409	456.563	20.690	1.0300

4.2.3 Kinetic deconvolutions in 85-DHS samples

Kinetic deconvolutions in 85-DHS samples are presented in Figure 8 for Gaussian transfer functions; and in Figure 9 for Weibull transfer functions. The difference in microstructural condition between this sample and the previous one is the presence in the latter of a larger number of defects due to a higher degree of deformation. In Figure 8, one out of the three reactions, the middle one in particular, prevails over the other two, whereas in Figure 9, with the Weibull transfer function, a first dominant reaction is observed interacting with a less prevailing one but whose enthalpy is larger than that of a second reaction obtained for samples cold-rolled to a lesser reduction.

Table 4 displays deconvolution parameters for 85-DHS samples, which are coherent with the aforesaid statement regarding Stotal and diffusive mechanisms.

There seems to be a setback, however, as total areas are compared with those of 50-DHS, perhaps a product of the rearrangement of dislocations occurring when a sample is severely deformed, although in the case of Weibull transfer functions, the area of the second reaction shows a gain in enthalpy relative to the first reaction, an expected behavior owing to the larger number of rolling defects in these samples.

4.3 Kinetic parameters

The following tables, 5, 6, and 7, present the temperature of the maximum for each reaction, the transfer function used, parameters n and m, the activation energy Q, linear determination factor R² (L), and the Arrhenius prefactor A.

The analysis of results must be carried out taking into account that the mechanisms of the resulting reactions are diffusive; that the diffusion energy of Si

in Al is 136 kJmol^{-1} in a temperature range between 480 and 620°C [58], capable of reaching 76 kJmol^{-1} between 360 to 500°C in thin foils [59]; that values between 135 and 223 kJmol^{-1} have been reported for diffusion of Fe in Al [60]; and also that for temperatures above 400°C , activation energy values from 79 to 184 kJmol^{-1} have been reported in

different reactions occurring in AA8011 under different microstructural conditions [61- 63].

The fitting results in Equation (1) are presented below, provided that the value R^2 is the one to generate the best theoretical-experimental correlation.

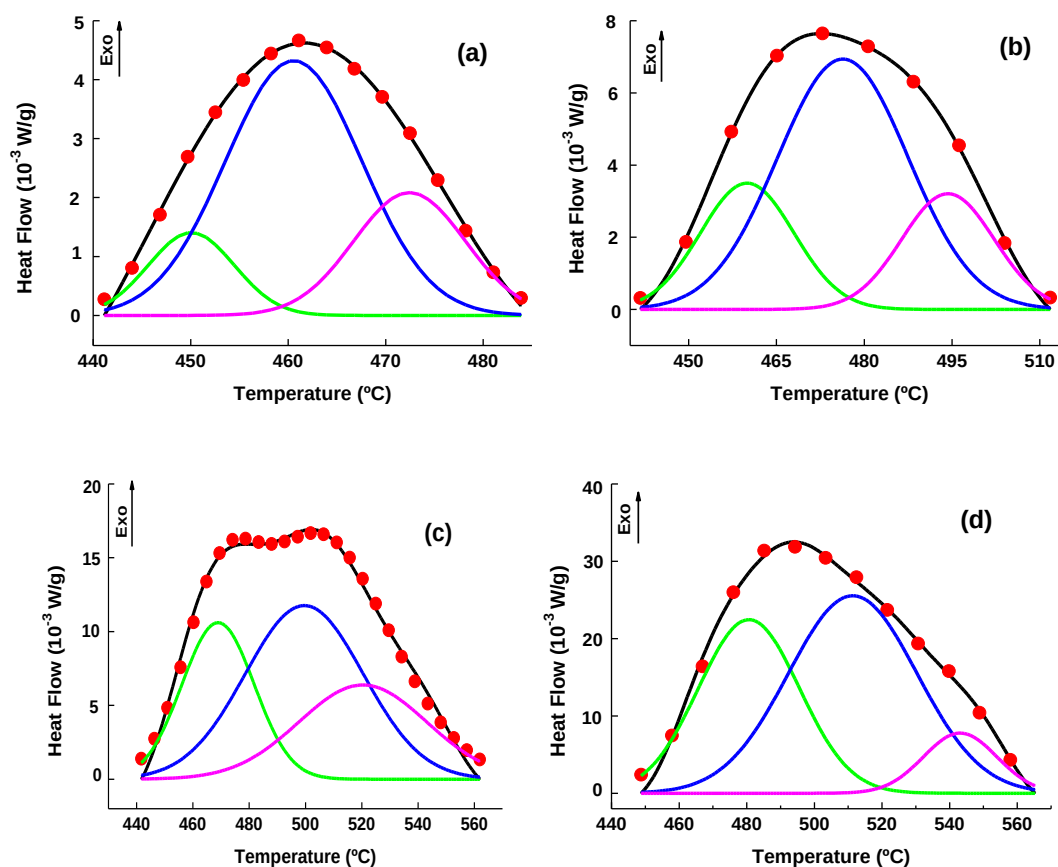


Figure 8. Deconvolution plots using Gaussian transfer function, showing the heat flow vs temperature for 85-DHS samples for different heating rates. a. 5°Cmin^{-1} b. 10°Cmin^{-1} c. 20°Cmin^{-1} d. 40°Cmin^{-1} .

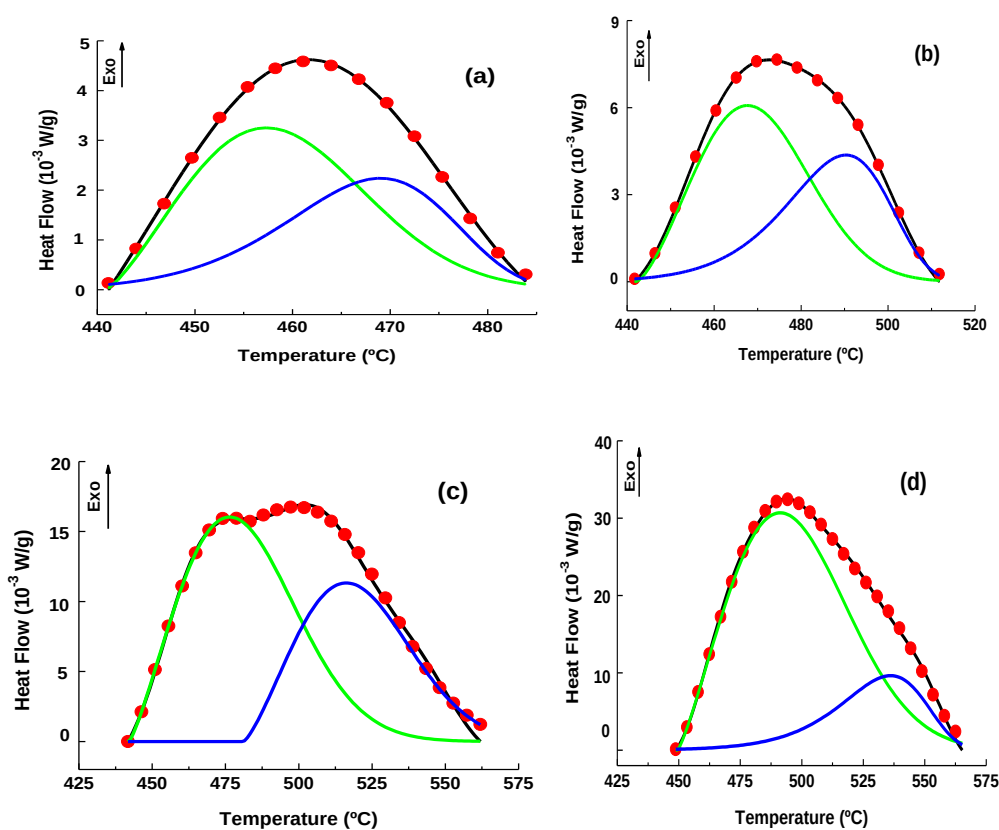
Table 4. Deconvolution parameters for Gaussian and Weibull transfer functions for AA8011 85-DHS samples.

β $^\circ\text{C min}^{-1}$	S_{Total}	R^2 TF	Reaction	W_0	W_1	W_2	W_3	S
5	0.12118	0.9979 G	1	0.0014054	450.062	4.41259		0.0155
			2	0.0043246	460.560	6.98770		0.0757
			3	0.0020851	472.445	5.71864		0.0299
10	0.32796	0.9987 G	1	0.0034999	459.992	7.99367		0.0701
			2	0.0069392	476.358	11.1634		0.1942
			3	0.0032096	494.313	7.91190		0.0637
20	1.32268	0.9925 G	1	0.0106065	468.943	12.8207		0.3409
			2	0.0117635	499.563	20.9540		0.6179

3 0.0063824 520.369 22.7499 0.3640

Table 4. Deconvolution parameters for Gaussian and Weibull transfer functions for AA8011 85-DHS samples. **Continued.**

β $^{\circ}\text{C min}^{-1}$	S_{Total}	R^2 TF	Reaction	W_0	W_1	W_2	W_3	S
40	2.26871	0.9950 G	1	0.0224553	480.649	14.9025		0.8388
			2	0.0255473	511.330	19.0217		1.2181
			3	0.0077900	543.114	10.8462		0.2118
5	0.12118	0.9987 W	1	0.0032529	457.304	21.04796	2.30422	0.0722
			2	0.0022396	469.010	71.97259	8.89100	0.0490
10	0.32694	0.9996 W	1	0.0060734	467.700	31.65814	2.46713	0.1292
			2	0.0043673	490.298	172.4429	15.1828	0.1345
20	1.31134	0.9965 W	1	0.0160366	476.412	44.80084	2.23006	0.7765
			2	0.0113294	516.225	44.85233	2.31111	0.5348
40	2.25400	0.9987 W	1	0.0306889	491.240	54.54027	2.22808	1.8102
			2	0.0096349	536.106	625.3847	36.8966	0.4438


Figure 9. Deconvolution plots using Weibull transfer function, showing the heat flow vs temperature for 85-DHS Samples for different heating rates. a. 5 °Cmin⁻¹ b. 10 °Cmin⁻¹ c. 20 °Cmin⁻¹ d. 40 °Cmin⁻¹.

4.3.1 Kinetic parameters for HS samples

Table 5 showcases the adjustment results for HS samples with both transfer functions, from which the following can be highlighted:

For Gaussian transfer functions, the first reaction holds values of n and m around 1 and 0.55, suggesting that the same kinetic function is valid for different β , akin to a sole mechanism with an activation energy reaching from 79 to 218 kJmol⁻¹. Values of n and m for the second reaction do not follow the same pattern as those of the first, two different types of kinetic functions being generated for $\beta=5$ and 10°C/min with activation energies over 400 kJ/mol; and for $\beta=20$ and 40°C/min with energies of 106 and 72 kJmol⁻¹, respectively. The third Gaussian reaction with $m=0$ shows a behavior associated to a reaction controlled by boundary diffusion, (Rn type with $n=1.4$ [43]). The activation energy values for this case are quite high, the $R^2(L)$ values being, in addition, the smallest obtained in the calculations. The asterisk indicates the existence of better $R^2(L)$ values, though their positive slopes bring forth an inconsistency with the value of Q . Reactions with high Q values are hardly harmonious with actual physical processes, an inconsistency that compromises the use of Gaussian transfer functions for the analysis of these experimental data.

For Weibull transfer functions, the first reaction shows values of $0.92 < n < 0.94$ and $0.47 < m < 0.51$, indicative of a sole kinetic function with an activation energy between 35 and 75 kJmol⁻¹, whereas a larger array of m values is obtained for the second reaction, showing that the data obtained at 5°C/min considerably pulls away from the single function presented by other β values. The activation energy for this reaction fluctuates between 36 and 109 kJmol⁻¹, these values being extremely low taking into account that this reaction occurs by Fe or Si diffusion.

4.3.2 Kinetic parameters for 50-DHS samples of an AA8011 alloy

Table 6 displays the results for 50-DHS samples for both transfer functions. The first reaction with the Gaussian transfer function shows similar n and m values for each β , and a decreasing activation energy with β located between 110 and 75 kJmol⁻¹. The second reaction equally presents a decreasing energy except for $\beta=40$ °C/min, where n and m differ from

those obtained for smaller β values. The third reaction presents equal n and m values within an elevated range and activation energy. Again, the asterisk in R2 indicates a possible adjustment with other kinetic parameters but with negative values of Q .

The Weibull distribution generates well behaved n and m values with a low activation energy between 30 and 56 kJ/mol for the first reaction, whereas for the second reaction a slight n and m dispersion is observed with Q values scattered around 206 kJmol⁻¹, these Q values being higher than those obtained with HS samples.

4.3.3 Kinetic parameters for 85-DHS samples

Table 7 showcases the kinetic parameters for 85-DHS samples. The first Gaussian reaction shows n and m values suggesting a kinetic function with decreasing Q values between 407 and 115 kJmol⁻¹ when β is increased. The second Gaussian reaction holds similar values of n and m except for $\beta=40$ °C/min, and a large Q dispersion; whereas in the third reaction, as in the two previous microstructures, the value of m remains zero, and Q values are quite high.

With Weibull, the first reaction reports energy values between 15 and 70 kJmol⁻¹; and the second, higher ones between 225 and 305 kJmol⁻¹.

This first kinetic analysis using only the fitting method of theoretical parameters on experimental data reveals that:

- The experimental kinetics are complex and separated into simple reactions by deconvolution, but no single criterion associates these simple reactions to each other for different values of β . Considering that the same physical mechanism should be represented by the same kinetic function, i.e., same values of n and m for the same mechanism, results show that different mechanism are responsible for the dispersion of Q values.
- As for the activation energy, an implicit dependence of ΔH on β subjects its value to both the natural logarithm of the experimental data's ratio and the kinetic function fitted on those data. The literature shows, for certain materials and for processes involving crystallization [45], a decreasing variation in Q as β grows; but there is

no mention in the literature of processes involving the coexistence of multiple mechanisms, so it is impossible to obtain the activation energy of any process without considering the experimental details, the sample geometry, and the heating rate β [47].

c) This method does not guarantee that the kinetic parameters obtained for a sequence of β values correspond to the same physical mechanism, hence the dispersion of Q values.

Table 5. Kinetic parameters for HS samples of an AA8011 alloy.

T (°C)	β °Cmin ⁻¹	TF- Reaction		n	m	Q kJmol ⁻¹	A	R ² (L)
436.008	5	G	1	0.945	0.595	79.2768	1.1052E+4	0.9999
445.181	10	G	1	0.945	0.615	113.233	2.0526E+6	0.9998
454.366	20	G	1	1.035	0.465	217.935	2.8275E13	0.9999
461.730	40	G	1	1.010	0.505	218.041	1.1191E13	0.9999
461.486	5	G	2	1.400	0.160	415.904	7.7168E27	0.9989
467.027	10	G	2	1.495	0.00	403.095	2.1746E26	0.9988
471.009	20	G	2	0.960	0.640	105.609	1.3329E+5	0.9991
476.483	40	G	2	0.910	0.680	72.4560	2.8206E+2	0.9997
484.419	5	G	3	1.400	0.00	469.113	3.7439E30	0.9975*
489.894	10	G	3	1.320	0.00	593.009	∞	0.9963*
494.361	20	G	3	1.420	0.00	473.335	6.8385E29	0.9980*
504.685	40	G	3	1.390	0.0	464.831	3.2496E28	0.9976*
437.141	5	W	1	0.920	0.465	35.3244	4.26894E0	0.9998
451.022	10	W	1	0.920	0.510	61.3737	1.9220E+2	0.9998
460.422	20	W	1	0.940	0.480	63.3537	1.1773E+2	0.9997
468.758	40	W	1	0.935	0.495	74.6479	3.5959E+2	0.9998
468.323	5	W	2	0.845	0.275	109.180	3.6507E+5	0.9998
480.933	10	W	2	0.740	0.700	36.2915	2.47504E0	0.9996
489.789	20	W	2	0.775	0.670	52.7781	1.3313E+1	0.9998
503.422	40	W	2	0.805	0.605	98.9312	7.4988E+3	0.9999

Table 6. Kinetic parameters for 50-DHS samples of an AA8011 alloy.

T (°C)	β °Cmin ⁻¹	TF- Reaction		n	m	Q kJmol ⁻¹	A	R ² (L)
448.700	5	G	1	0.985	0.540	110.266	1.6109E+6	0.9999
462.520	10	G	1	0.955	0.590	109.140	5.5989E+5	0.9993
471.227	20	G	1	0.915	0.660	75.5929	9.8593E+2	0.9998
482.661	40	G	1	0.940	0.605	74.9811	2.7030E+2	0.9999
468.560	5	G	2	1.105	0.495	295.724	1.8845E19	0.9989
484.110	10	G	2	1.125	0.460	215.559	7.0397E12	0.9989
499.744	20	G	2	1.040	0.355	115.597	2.0768E+5	0.9989
521.404	40	G	2	1.475	0.00	306.818	1.8999E17	0.9989

Table 6. Kinetic parameters for 50-DHS samples of an AA8011 alloy. **Continued.**

T (°C)	β °Cmin ⁻¹	TF- Reaction	n	m	Q kJmol ⁻¹	A	R ² (L)
482.370	5	G 3	1.455	0.00	606.257	∞	0.9982*
511.240	10	G 3	1.360	0.00	459.806	3.1981E28	0.9974*
531.297	20	G 3	1.435	0.00	558.783	8.6309E33	0.9979*
553.430	40	G 3	1.380	0.00	491.405	2.0958E28	0.9975*
453.450	5	W 1	0.850	0.50	34.0441	2.86693E0	0.9974
471.360	10	W 1	0.920	0.515	55.5770	4.6490E+2	0.9998
491.960	20	W 1	0.845	0.570	30.2830	2.6719E-1	0.9999
512.057	40	W 1	0.830	0.595	32.8639	1.4727E-1	0.9999
483.210	5	W 2	0.890	0.565	128.629	2.1354E+7	0.9998
505.730	10	W 2	1.130	0.00	282.513	4.5579E16	0.9980
525.020	20	W 2	0.910	0.250	211.173	1.8366E11	0.9999
544.409	40	W 2	0.920	0.135	202.513	9.3904E+9	0.9999

Table 7. Kinetic parameters for 85-DHS samples of an AA8011 alloy.

T (°C)	β °Cmin ⁻¹	TF Reaction	n	m	Q kJmol ⁻¹	A	R ² (L)
450.060	5	G 1	1.025	0.490	407.448	1.4162E28	0.9999
459.990	10	G 1	0.965	0.585	166.892	1.1511E10	0.9999
468.840	20	G 1	1.000	0.515	135.669	1.5962E+7	0.9999
480.649	40	G 1	0.990	0.525	115.323	1.8977E+5	0.9999
460.560	5	G 2	0.905	0.700	109.210	2.0905E+6	0.9994
476.360	10	G 2	0.990	0.600	140.628	6.8578E+7	0.9989
499.560	20	G 2	0.875	0.705	33.8929	5.6063E-1	0.9992
511.330	40	G 2	1.470	0.00	343.829	1.1530E20	0.9988*
472.440	5	G 3	1.440	0.00	1077.99	∞	0.9978*
494.310	10	G 3	1.420	0.00	807.485	∞	0.9973*
520.370	20	G 3	1.185	0.00	268.900	1.0844E15	0.9954*
543.115	40	G 3	1.310	0.00	638.310	1.6980E38	0.9957*
457.303	5	W 1	0.840	0.525	57.3963	2.8825E+2	0.9984
467.700	10	W 1	0.905	0.525	69.5353	6.6204E+2	0.9998
476.410	20	W 1	0.930	0.485	46.9284	0.4888E0	0.9998
491.240	40	W 1	0.820	0.530	14.8788	1.0970E-2	0.9994
469.010	5	W 2	0.790	0.520	224.620	1.6024E14	0.9998
490.300	10	W 2	0.865	0.380	250.365	1.2061E15	0.9979
516.230	20	W 2	1.330	0.000	305.189	3.5790E17	0.9987
536.104	40	W 2	0.880	0.175	246.916	1.2233E13	0.9999

4.4 Activation energy evaluation

This section combines isoconversion theory tenets and experimental kinetic deconvolution results obtained via calorimetric measurements for HS, 50-DHS, and 85-DHS samples [48,65,66]. Peak temperatures for different values of β are identified from the deconvolved curves, and the activation energy Q is evaluated using the isoconversion relation (Equation (2)) [48].

Columns 1 and 2 from Tables 5, 6, and 7, for HS, 50-DHS and 85-DHS samples respectively, show the temperature of the maximum of each deconvolved reaction and its respective heating rate β . From these values, $\ln(\beta/T^2)$ vs $1/T$ was plotted, the slope ($-Q/R$) and intercept $\ln(A)$ being determined next. Figure 10 displays the respective Kissinger plots, and Table 8 showcases the different parameters deduced from them.

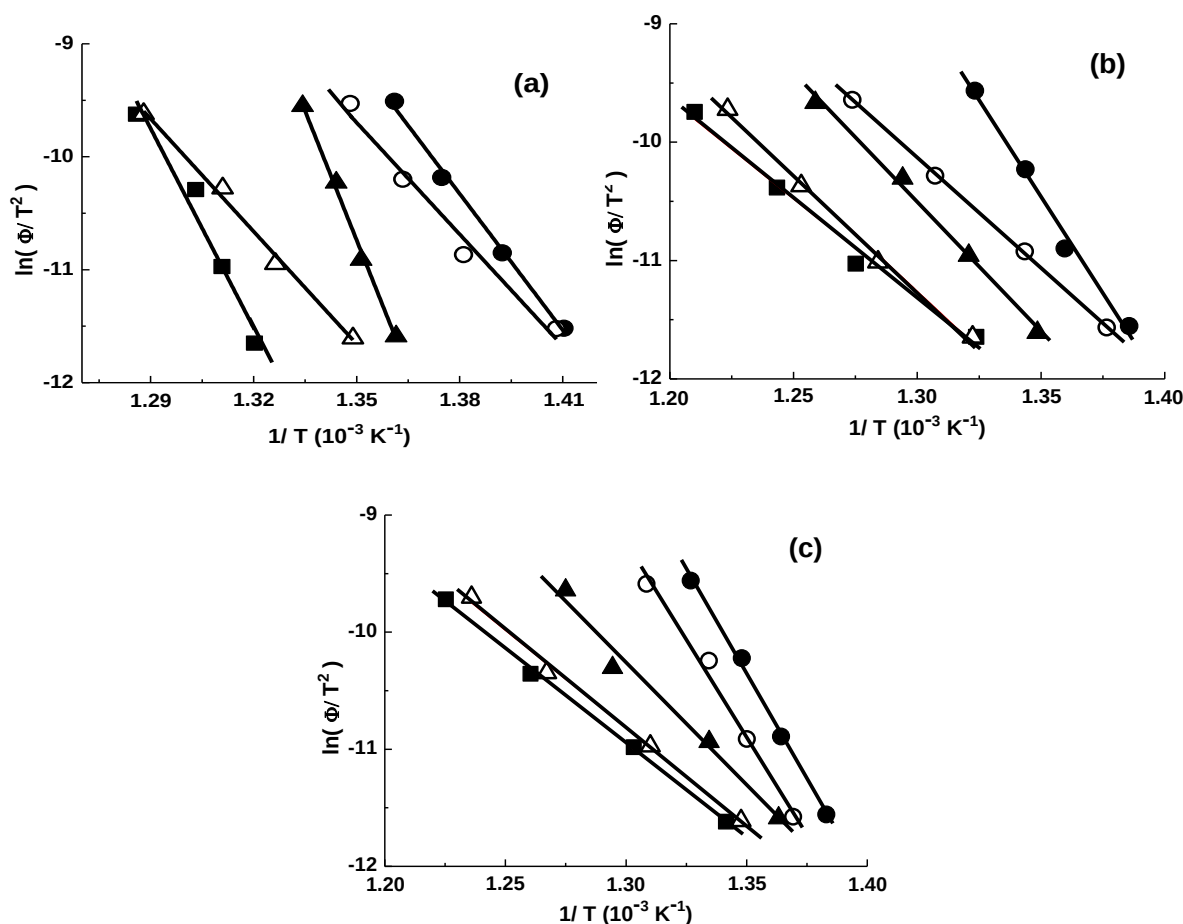


Figure 10. Kissinger plots to determine activation energy Q for different reactions deconvolved in an AA8011 alloy. a) Samples HS b) Samples 50-DHS c) Samples 85-DHS. Black symbols: Using Gaussian TF. White symbols: Using Weibull TF. Circle: First reaction. Triangle: Second reaction. Square: Third reaction.

The linearity obtained for each reaction and for every one of the microstructures studied was exceptionally good, which is reflected in values of $R^2 \geq 0.99$, except in the case of the third reaction using HS samples with Gaussian transfer functions. Comparing these energies with those obtained in the previous section via linear regression, where the same reaction with

different values of β reflects important differences, makes for the conclusion that the supposed fitting uniqueness of parameters is not so; and that different sets of parameters that minimize Equation (1), for example, might be obtained. The more adjustable parameters exist, the more groups of these parameters might achieve such minimization. Based on this

reasoning, it is necessary to reduce the group of parameters minimizing Equation (1), so that the n and m dispersion can be made smaller, and thus the Q energy spectrum obtained in the previous section be in turn lessened. The energy values obtained by isoconversion are located between 139 and 489 kJmol⁻¹, excepting the value of 633 kJmol⁻¹, reached by the second reaction in HS samples using Gaussian transfer function, which can be better explained by

taking into account that these reactions are diffusive, and that the diffusion energy of the main alloying components in AA8011 are 136 kJmol⁻¹ for Si in Al and up to 232 kJmol⁻¹ for Fe in Al. In conclusion, isoconversion allows for more reliable energy values, and reduces the uncertainty regarding the values fitting the kinetic function; hence the need to apply an isoconversion assessment before evaluating the parameters of the latter.

Table 8. Activation energy and other parameters deduced from the linearization of Equation 8.

Samples	Reaction	TF	Slope	Ln(A)	R ²	Q (kJmol ⁻¹)
HS	1	G	-40.231	45.192	0.994	334.493
HS	2	G	-76.122	90.029	0.998	632.901
HS	3	G	-58.840	66.154	0.982	489.214
HS	1	W	-32.956	34.793	0.990	282.321
HS	2	W	-33.236	33.211	0.997	276.128
50-DHS	1	G	-32.407	33.286	0.995	269.442
50-DHS	2	G	-21.179	17.820	0.997	176.089
50-DHS	3	G	-16.788	10.505	0.994	139.581
50-DHS	1	W	-18.606	14.054	0.999	154.713
50-DHS	2	W	-19.480	14.066	0.997	161.963
85-DHS	1	G	-35.967	38.196	0.999	317.573
85-DHS	2	G	-20.873	16.869	0.991	173.545
85-DHS	3	G	-16.131	10.020	0.994	134.118
85-DHS	1	W	-33.131	33.834	0.994	275.461
85-DHS	2	W	-16.708	10.899	0.998	138.915

4.5 Kinetic parameters deduced from isoconversion and SB combined methods

The activation energy having been evaluated through isoconversion, Q_{iso} , there followed the evaluation of the kinetic function, applying the same methodology as in the previous section, but in this case, seeking the values of n and m linearizing Eq. (7) for a value of activation energy equal to the energy obtained by isoconversion. A well-behaved kinetic function for n and m is that which generates the highest $R^2(L)$ value for a Q value no more than 0.5% apart from Q_{iso} .

The parameters obtained through linear regression for homogenized samples (HS) are shown in Table 9. It shows activation energy values obtained by isoconversion (Q_{iso}) and those obtained by adjustment (Q_{SB}), as well as n and m values of the A Šesták-Berggren kinetic function and the R^2

correlation factor quotient for each transfer function used.

Q values obtained using Gaussian transfer functions are higher than those obtained using Weibull. Undoubtedly, Q values obtained for reactions 1 and 2 with Weibull may be interpreted as having been mainly generated, in lesser proportion, by Fe and Si diffusion, where undoubtedly Fe and Si rich phases coexist, possibly those of α -AlFeSi and Al₃Fe, in agreement with reports by Shoji [29]. A graceful way to circumvent elaboration regarding the high values obtained when the Gaussian transfer function is used, is accepting that it is inadequate for the kinetics study of these particular experimental data. Even A values are much too high for the third reaction.

Table 10 shows the results for 50-DHS samples. In this case, Q values displayed seem valid for both

Gaussian and Weibull transfer functions. It must be taken into account that these samples are cold-rolled down to 50%; that the recrystallization process at this temperature has been completed or is in the process of being completed; and that an extra mechanism, associated to recrystallized grain growth, must be under way. The energy of the first two reactions using Gaussian transfer functions indicates that a process is indeed ongoing, whereby Fe diffusion is

predominant, and Si diffusion markedly less so; whereas the third reaction might well correspond to the high-angle boundary migration that characterizes crystallized grain growth. Using Weibull transfer functions results in Q values much lower than those reported for homogenized samples, though bearing more resemblance to those of reactions 2 and 3 obtained with Gaussian transfer functions.

Table 9. Kinetic parameters deduced from combined Isoconversion-Šesták-Berggren models, for HS samples.

$Q=Q_{SB}$ kJmol ⁻¹	β (°C/min)	TF Reaction	n	m	$Q=Q_{ISO}$ kJmol ⁻¹	A	R ² (L)
333.773	5	G 1	1.435	0.065	334.493	5.9271E22	0.9991
333.451	10	G 1	1.230	0.320		2.1085E22	0.9993
334.999	20	G 1	1.170	0.335		7.1945E21	0.9997
334.277	40	G 1	1.130	0.390		2.0529E21	0.9997
630.376	5	G 2	1.870	0.000	632.901	∞	0.9952
630.601	10	G 2	2.310	0.000		∞	0.9842
631.487	20	G 2	1.865	0.000		∞	0.9951
630.834	40	G 2	1.865	0.000		∞	0.9951
487.187	5	G 3	1.455	0.00	489.214	6.9966E31	0.9973
490.358	10	G 3	1.210	0.130		3.8453E31	0.9959
486.835	20	G 3	1.460	0.00		5.9149E30	0.9978
488.452	40	G 3	1.460	0.0		1.3500E30	0.9973
281.417	5	W 1	1.655	0.000	282.321	4.9628E18	0.9978
282.314	10	W 1	1.375	0.145		1.5466E18	0.9984
281.851	20	W 1	1.390	0.165		4.0843E18	0.9982
282.174	40	W 1	1.305	0.205		1.4089E17	0.9986
274.999	5	W 2	1.680	0.000	276.128	4.0348E17	0.9746
275.239	10	W 2	1.095	0.220		8.6970E16	0.9986
275.098	20	W 2	1.135	0.125		2.1441E16	0.9989
275.220	40	W 2	1.050	0.150		5.2519E13	0.9995

Table 11 displays kinetic parameters for 85-DHS, where the behavior obtained in moderately deformed samples is emphasized. The activation energy shows two reactions, the first for each transfer function might well be associated to an Fe-rich phase precipitation, whether Fe₃Al or β -AlFeSi; whereas the third Gaussian reaction and the second Weibull reaction coincide in energy value, in agreement with the high-angle boundary diffusion

referenced in [2,51,67]. The Q value for the second reaction using Gaussian transfer function coincides with that obtained for 50-DHS samples.

This second kinetic analysis reveals n and m dispersion values lower than those obtained using the previous method. This dispersion is attributable to the dependence of the activation energy Q on α , and to the fact that the Kissinger method used can only be considered as an isoconversion method for

fully symmetric kinetic reactions where the T_p value corresponds to a conversion around $\alpha = 0.5$, this

being valid when Gauss transfer functions are used, but not when using Weibull functions.

Table 10. Kinetic parameters deduced from combined Isoconversion-Šesták-Berggren models, for 50-DHS samples.

$Q=Q_{SB}$ kJmol^{-1}	β° Cmin^{-1}	FT Reaction	n	m	$Q=Q_{iso}$ kJmol^{-1}	A	R^2
268.296	5	G 1	1.260	0.250	269.442	4.3248E17	0.9994
268.739	10	G 1	1.185	0.345		1.1879E17	0.9994
269.463	20	G 1	1.200	0.355		3.9162E16	0.9992
269.206	40	G 1	1.305	0.200		6.9225E15	0.9993
176.707	5	G 2	0.990	0.625	176.089	8.0954E10	0.9989
176.619	10	G 2	1.070	0.525		1.4603E10	0.9989
175.305	20	G 2	1.160	0.395		2.2246E09	0.9989
176.198	40	G 2	1.190	0.345		5.1125E08	0.9988
140.093	5	G 3	0.935	0.615	139.581	1.0787E08	0.9967
139.137	10	G 3	0.925	0.545		1.5004E07	0.9940
138.884	20	G 3	0.925	0.595		4.8655E06	0.9951
139.494	40	G 3	0.920	0.560		1.2703E06	0.9941
155.471	5	W 1	1.175	0.235	154.713	1.4679E09	0.9972
154.441	10	W 1	1.150	0.315		3.9031E08	0.9989
154.724	20	W 1	1.175	0.245		7.9783E07	0.9983
154.250	40	W 1	1.170	0.190		1.6677E07	0.9986
161.421	5	W 2	0.920	0.535	161.963	3.9153E09	0.9997
162.316	10	W 2	0.925	0.340		4.0651E08	0.9984
162.042	20	W 2	0.850	0.415		1.1435E08	0.9995
162.063	40	W 2	0.865	0.300		2.5104E07	0.9999

Table 11. Kinetic parameters inferred from combined Isoconversion-Šesták-Berggren models for 85-DHS samples.

$Q=Q_{SB}$ kJmol^{-1}	β $^\circ\text{Cmin}^{-1}$	TF Reaction	n	m	$Q=Q_{iso}$ kJmol^{-1}	A	R^2
319.118	5	G 1	0.975	0.540	317.573	5.9073E20	0.9998
317.853	10	G 1	1.115	0.430		6.5345E20	0.9996
317.201	20	G 1	1.280	0.225		9.4382E19	0.9994
316.827	40	G 1	1.340	0.160		1.7131E19	0.9993
173.645	5	G 2	0.960	0.640	173.545	8.0643E10	0.9993
173.147	10	G 2	1.030	0.550		1.2565E10	0.9989
172.878	20	G 2	1.185	0.340		1.3433E09	0.9989
173.837	40	G 2	1.140	0.400		5.7934E08	0.9987

Table 11. Kinetic parameters inferred from combined Isoconversion-Šesták-Berggren models for 85-DHS samples. Continued.

Q=QSB kJmol ⁻¹	β °Cmin ⁻¹	TF Reaction	n	m	Q=Q _{iso} kJmol ⁻¹	A	R ²
134.492	5	G 3	0.815	0.695	134.118	1.0896E08	0.9848
134.756	10	G 3	0.865	0.670		2.2302E07	0.9873
134.434	20	G 3	0.915	0.375		1.5953E07	0.9918
134.165	40	G 3	0.825	0.610		9.7962E05	0.9817
274.243	5	W 1	1.110	0.310	275.461	8.9681E17	0.9977
274.380	10	W 1	1.255	0.240		1.7907E17	0.9985
274.705	20	W 1	1.525	0.020		3.3228E16	0.9982
274.296	40	W 1	1.670	0.000		6.0538E15	0.9960
139.006	5	W 2	0.725	0.645	138.915	1.5129E08	0.9993
139.565	10	W 2	0.765	0.625		3.2357E07	0.9996
138.948	20	W 2	0.980	0.300		3.7609E06	0.9921
139.364	40	W 2	0.765	0.525		1.4631E06	0.9999

5. CONCLUSIONS

An above-400°C study of an Al-Fe-Si alloy (AA8011) was carried out by calorimetric curve deconvolution obtained by DSC using different transfer functions and by combining Šesták-Berggren and isoconversion methods, with the following conclusions:

1. A kinetic analysis based solely on the adjustment of parameters associated to the kinetic function does not guarantee the absolute minimum demanded by linear regression, so that different relative minima that meet the condition of linearity may be obtained. The isoconversion method, by directly supplying the activation energy, reduces this problem to obtaining the kinetic function that replicates that energy value.
2. The deconvolution of experimental DSC plots by employing Gaussian and Weibull functions evinces the coexistence of different overlapping reactions happening along the main processes and affecting their kinetic parameters. It took three reactions to reproduce the experimental kinetic when using Gaussian transfer function, whereas only two were needed when Weibull functions were used. This is possible since the asymmetry associated to Weibull better covers the start and endpoints of the experimental kinetic.
3. In the case of homogenized samples, the Gaussian transfer function results in physically inadequate outcomes, whereas the Weibull transfer function predicts the coexistence of two Fe-rich phases, the first of which corresponds, according to the literature, to AlFeSi; and the second, probably, to Al₃Fe [29,30].
4. For highly deformed samples, Gaussian transfer functions predict two reactions whose activation energy is in agreement with Fe diffusion energy; whereas the third reaction reflects activation energy in conformity with the energy associated to the diffusion process of high-angle grain boundaries. Weibull transfer functions yield an Fe-rich phase and a second reaction associated to the diffusion process of grain boundaries located around 136 kJmol⁻¹, similar value for both transfer functions.
5. It follows that in multicomponent alloys, DSC measurements generate a heat flow which in turn encompasses several reactions; and the particular information borne by each of them can be inferred by using deconvolution methods.

6. The combination of isoconversion and linear regression are presented as the adequate methodology to determine the kinetic triplet.

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8. APENDIX

Derivation of equation (1)

The reaction rate taken from the theory of chemical reactions for isothermal processes is given by

$$\frac{d\alpha}{dt} = K(T)F(\alpha) \quad (A1)$$

Considering the heating ratio $\beta = dT/dt$, this same expression can be used for non-isothermal processes,

$$\beta \frac{d\alpha}{dT} = K(T)F(\alpha) \quad (A2)$$

Experimentally, the extension of the conversion or transformed fraction α , associated with the reaction, can be deduced from the heat flow curve as a function of time considering that in the isothermal case α is defined, by:

$$\alpha = \frac{\int_0^{t_\alpha} \Delta H dt}{\int_0^{t_f} \Delta H dt} \quad (A3)$$

And in the non-isothermal case

$$\alpha = \frac{\int_0^{T_\alpha} \Delta H dT}{\int_0^{T_f} \Delta H dT} \quad (A4)$$

where t_α (T_α) represents the time (Temperature) elapsed for the reaction to reach a transformed fraction α and t_f (T_f) the time (Temperature) for the reaction to occur completely. The integral of the denominator represents the total area under the curve and we designate it with the letter S. Deriving α in A3 with respect to time (A4 with respect to Temperature) we obtain the relation

$$\frac{d\alpha}{dt} = \frac{\Delta H_\alpha}{S} \quad (A5)$$

$$\frac{d\alpha}{dT} = \frac{\Delta H_\alpha}{S'} \quad (A6)$$

Note that in A6 the area is written as S' to differentiate the gauging unity from that at A5. Combining A1 and A5 in the isothermal case, and A2 with A6 for the non-isothermal case, we obtain:

$$\frac{d\alpha}{dt} = K(T)F(\alpha) = \frac{\Delta H_\alpha}{S} \quad (A7)$$

$$\frac{d\alpha}{dT} = \frac{K(T)F(\alpha)}{\beta} = \frac{\Delta H_\alpha}{S'} \quad (A8)$$

considering that the reaction constant follows an Arrhenius relationship, $K(T)$ is defined as

$$K(T) = A \exp\left(-\frac{Q}{RT}\right) \quad (A9)$$

And that the kinetic function $F(\alpha)$ in the two-parameter model of Šesták -Berggren is defined by:

$$F(\alpha) = (1 - \alpha)^n \alpha^m \quad (A10)$$

For the isothermal case, the expressions A9 and A10 are substituted in A7 and the neperian logarithm is taken, generating Equation (1)

$$\ln\left(\frac{\Delta H_\alpha}{S(1-\alpha)^n \alpha^m}\right) = \ln(A) - \frac{Q}{RT} \quad (1)$$

While that expression, following the same procedure, in the non-isothermal case, is written as

$$\ln\left(\frac{\beta \Delta H_\alpha}{S'(1-\alpha)^n \alpha^m}\right) = \ln(A) - \frac{Q}{RT} \quad (A11)$$

Note that both (1) and (A11) have similar functional forms when we incorporate in A11 the term $\ln(\beta)$ into the term $\ln(A)$ and define $A' = A / \beta$.

9. SYMBOL LIST

ΔH : Heat flow

S: Area under the heat flow curve

α : Fraction transformed, conversion extension

$F(\alpha)$: Kinetic function

$K(T)$: Reaction constant

n, m : Coefficients of Šesták -Berggren

A: Arrhenius prefactor

Q: Apparent activation energy

Q_{SB} : Activation energy deduced from the Šesták-Berggren model

Q_{iso} : Activation energy deduced from the isoconversion scheme

R: Universal gas constant

T: Temperature

t: Time

β : Heating rate

R^2 : Determination coefficient of the regression

N: Validation coefficient of the Isoconversion

X (t): Input signal

Y (t): Output signal

g (t): General transfer function

W: Gauss or Weibull transfer function

Wi: Transfer function parameters

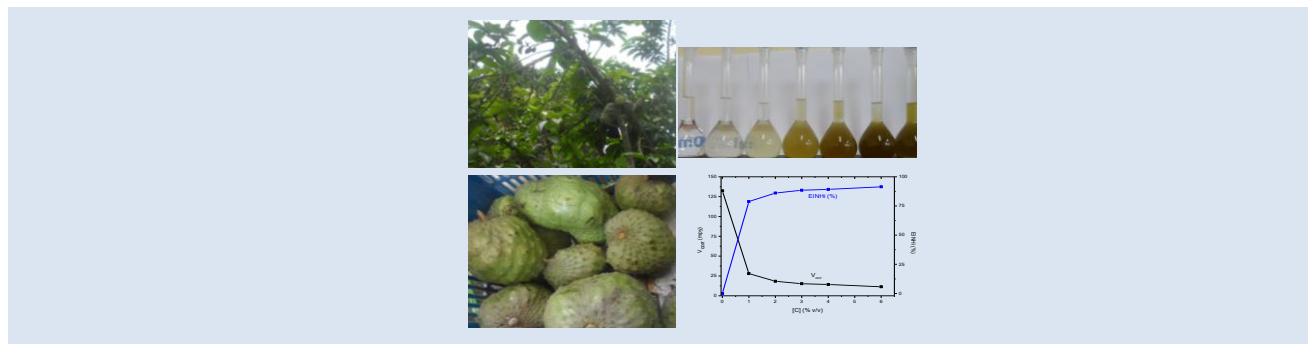
S_{Total} : Total area, sum of area for each deconvolved reaction

TF: Type of transfer function (G: Gauss; W: Weibull)

EVALUACIÓN DE LA INHIBICIÓN DE LA CORROSIÓN DEL ACERO EN MEDIO ÁCIDO USANDO EL EXTRACTO DE CÁSCARAS DE *ANNONA MURICATA L.*Abel Vergara^{1*}, Karin Paucar¹, Pedro Pizarro¹, Ronald Paucar¹, I. Silupú¹

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RESUMEN

En este trabajo de investigación se reporta los resultados obtenidos de la evaluación del efecto inhibitor de la corrosión del extracto etanólico obtenido a partir de las cáscaras del fruto de la *Annona muricata L.* por medio de las técnicas gravimétrica (pérdida de peso), electroquímica (polarización potenciodinámica) y microscopía electrónica de barrido (MEB). Las pruebas se realizaron usando acero SAE 1008 en medio ácido (HCl 0,5M) en ausencia y presencia del inhibidor. El inhibidor se evaluó a cinco diferentes concentraciones de 1-6 %v/v. Los resultados preliminares obtenidos indican que con el incremento de la concentración del extracto inhibitor la velocidad de corrosión del acero disminuye y que la eficiencia de inhibición aumenta alcanzando valores próximos al 90%. Los resultados de pérdida de peso y electroquímicos muestran que su mecanismo de inhibición se debe a la adsorción de moléculas del inhibidor sobre el metal, la cual correlaciona con la isoterma de adsorción de Langmuir. El análisis superficial por MEB de las muestras de acero después de su inmersión en solución de HCl 0,5M en presencia del extracto inhibitor evidenció una mejora en su acabado superficial respecto al ataque en ausencia del mismo, confirmando así la capacidad inhibitor de la corrosión del extracto.

Palabras claves: inhibitor, cáscaras de *Annona muricata L.*, curvas de polarización, pérdida de peso.

EVALUATION OF THE CORROSION INHIBITION OF STEEL IN ACID MEDIUM USING THE EXTRACT OF *ANNONA MURICATA L.* PEELS

ABSTRACT

In this research the results of the evaluation of corrosion inhibition effect of an ethanolic extract obtained from the fruit peels of *Annona muricata L.* by means of gravimetric (weight loss) and electrochemical (potentiodynamic polarization) techniques and microscopy SEM are reported. The tests were performed using steel SAE 1008 in acid medium (HCl 0.5M) in absence and presence of the inhibitor. The corrosion inhibitor was tested in five different concentrations of 1-6% v/v. The results indicate that with the increase of the inhibitor extract concentration the corrosion rate of steel decreases and the inhibition efficiency increases reaching values close to 90%. All weight loss and electrochemical results show that their inhibition mechanism is due to the adsorption of inhibitor molecules on the metal, which followed a Langmuir adsorption isotherm. The SEM analysis of the steel samples after their immersion in HCl 0.5M solution in the presence of the inhibitor extract evidenced an improvement in their surface finish compared to the attack in their absence, confirming their ability to inhibit the corrosion of the extract.

Key words: inhibitor, peels of *Annona muricata L.*, polarization curves, weight loss.

1. INTRODUCCIÓN

Un método eficaz y económico para el control y prevención de la corrosión del acero en medio ácido es el uso de inhibidores [1]. Los extractos obtenidos a partir de diferentes partes de las plantas (hojas, frutos, semillas, cáscaras, etc.) han revelado su efecto inhibitorio de la corrosión debido a la presencia de compuestos fenólicos, flavonoides, alcaloides, taninos, etc.; en general, compuestos orgánicos de cadenas gobernadas con enlaces simples, dobles, triples, anillos aromáticos y heteroátomos como N, O y S, que pueden absorberse sobre el acero debido al enlace que puede resultar por su interacción con los electrones p y/o π así como con los electrones libres de los átomos donadores y que actuando como una especie barrera reduce su ataque por corrosión cuando es expuesto al medio ácido [2-5]. En particular, los extractos de las cáscaras de frutos de una variedad de plantas tales como mango, naranja, plátano, entre otros, han reportado aceptables propiedades inhibitorias de la corrosión del acero en soluciones ácidas [5-9]. Por ejemplo, Xue-Fan et al. [5] verificaron que el extracto obtenido a partir de la cáscara de granada en HCl 1M a una concentración de 500 mg/L alcanzó una eficiencia de 93% a 30°C mientras que Taleb et al. [8] reportaron una eficiencia de inhibición del 84% en HCl 2M a 25°C a 1000 ppm de concentración del extracto de las cáscaras de papa.

La *Annona muricata* L. es una planta que pertenece a la familia de la *Annonaceae*, los extractos obtenidos a partir de sus diferentes partes: hojas, cáscaras y semillas han reportado la presencia de metabolitos secundarios como: fenoles, alcaloides, flavonoides, taninos, entre otros, que les aportan actividad biológica, insecticida, antimicrobial, anticorrosiva, etc. [10-14].

El presente trabajo es el primer reporte sobre la aplicación del extracto etanólico de las cáscaras del fruto de la *Annona muricata* L. como inhibidor de la corrosión del acero SAE 1008 en solución ácida de HCl 0,5M a diferentes concentraciones del extracto. La eficiencia de inhibición de la corrosión fue determinada por ensayos de pérdida de peso y polarización potenciodinámica. La morfología superficial fue examinada por microscopía electrónica de barrido (MEB).

2. PARTE EXPERIMENTAL

2.1 Obtención del extracto inhibitorio

Las cáscaras secas de *Annona muricata* L. fueron molidas y tamizadas hasta malla N°10 (2 mm). La extracción se obtuvo usando 30 g. de cáscaras en 100 mL de etanol absoluto, Merck p.a. usando agitación constante durante 2h y posterior filtración al vacío. El extracto así obtenido fue caracterizado a través de marcha fitoquímica [15,16] y medición del contenido de alcaloides [16] y flavonoides [17].

2.2 Electrodo de trabajo y solución de ensayo

Se utilizaron muestras rectangulares de un acero SAE 1008 (0,04% C, 0,01% Si, 0,18% Mn, 0,018% P, 0,007% S, 0,029% Al, 0,0008% B, resto % Fe), que previamente fueron tratadas mediante un desbaste sucesivo con papel abrasivo de mallas 80 a 1000, lavadas con agua destilada, limpiadas en ultrasonido con etanol y secadas antes de ser pesadas. Este tratamiento de las muestras de acero se utiliza tanto para el ensayo gravimétrico como para el ensayo electroquímico. La solución de ensayo HCl 0,5 M se preparó a partir de la dilución de HCl 37% p.a. y agua destilada.

2.3 Ensayos gravimétricos

La velocidad de corrosión de las muestras de acero SAE 1008 en HCl 0,5 M en ausencia y presencia del extracto etanólico de cáscaras de *Annona muricata* L. se determinó a temperatura ambiente a partir de la inmersión de muestras rectangulares de 40 x 10 x 2 mm en la solución corrosiva naturalmente aereada. Las muestras ya tratadas por desbaste fueron suspendidas en la solución de ensayo. Transcurrido el tiempo de inmersión de 2h, las muestras fueron retiradas y lavadas con agua destilada, etanol, secadas y pesadas. Los experimentos se realizaron por triplicado y con reproducibilidad. El rango de concentración del extracto etanólico de la planta *Annona muricata* L. empleado en la evaluación fue del 1 al 6 %v/v. Todos los ensayos se realizaron a temperatura ambiente (294 K). La concentración del inhibidor se expresó en %v/v, la eficiencia de inhibición η (%) y superficie cubierta (θ) se determinaron usando las siguientes relaciones [18,19]:

$$\eta = (\Delta m_o - \Delta m_i) / \Delta m_o \times 100 \quad (1)$$

Donde: Δm_o y Δm_i son las pérdidas de masas entre el área de las muestras (cm^2) en ausencia y en

presencia del inhibidor, respectivamente.

$$\Theta = 1 - \Delta m_i / \Delta m_o \quad (2)$$

Para poder determinar la velocidad de corrosión en mpy (milésima de pulgada por año) se utilizó la siguiente relación:

$$\text{Velocidad de corrosión (mpy)} = K \Delta m A^{-1} T^{-1} D^{-1} \quad (3)$$

Donde:

Δm pérdida de masa en g

A área de la muestra en cm^2

T tiempo de inmersión en horas

D densidad del acero 7,86 g/cm^3

$$K = 3,45 \times 10^6$$

2.4 Ensayos electroquímicos

2.4.1. Curvas de polarización potenciodinámica

Las curvas de polarización potenciodinámica se realizaron usando una celda de tres electrodos. Esta celda consistió de una muestra de acero SAE 1008 previamente tratada como electrodo de trabajo, de una placa plana de platino como electrodo auxiliar y un electrodo de calomel saturado (SCE) como electrodo de referencia. Antes de polarizar la muestra, se realizó la medición del potencial del circuito abierto (OCP) del electrodo de trabajo, el cual fue registrado durante 1h. Las curvas de polarización se obtuvieron a partir de la polarización del electrodo de trabajo en el rango de -20 a +20 mV a una velocidad de barrido de 0,5 mV/s para determinar la resistencia a la polarización, R_p . Las curvas de polarización para el rango de -250 a +250 mV a una velocidad de barrido de 1 mV/s permitieron determinar las pendientes de tafel, potencial de corrosión (E_{corr}) y la densidad de corriente de corrosión (i_{corr}). Las curvas de polarización se obtuvieron usando un potencióstato AUTOLAB 302N. La eficiencia de inhibición η (%) se determinó usando las siguientes relaciones:

$$\eta (\%) = (i_{\text{corr } o} - i_{\text{corr } i}) / i_{\text{corr } o} \times 100 \quad (4)$$

Donde:

$i_{\text{corr } o}$ y $i_{\text{corr } i}$ son la densidad de corriente de corrosión en ausencia y en presencia del inhibidor, respectivamente.

2.5 Morfología superficial

Las muestras de acero SAE 1008 inmersas en solución HCl 0,5M en ausencia y presencia del extracto inhibidor a partir de las cáscaras de *Annona*

muricata L. por 2h a temperatura ambiente, fueron lavadas con agua, secados con etanol y almacenados en desecador hasta su evaluación. Las imágenes morfológicas superficiales fueron obtenidas usando un microscopio electrónico Carl Zeiss de barrido (MEB), EVO MA15 a 1500X, con detector de electrones retrodispersados sonda EDS.

3. RESULTADOS Y DISCUSIÓN

3.1 Caracterización del extracto inhibidor

La marcha fitoquímica del extracto etanólico de las cáscaras de *Annona muricata* L. muestra la presencia de alcaloides, taninos, fenoles y flavonoides, mayoritariamente, ver Tabla 1. La determinación cuantitativa de algunos metabolitos identificados cualitativamente, se lista en la Tabla 2.

Tabla 1. Marcha Fitoquímica del extracto etanólico de cáscaras de *Annona muricata* L.

Ensayo	Extracto etanólico de cáscaras de <i>Annona muricata</i> L.
Alcaloides	
Reacción de Mayer	+
Reacción de Dragendorff	++
Reacción de Bouchardat	+
Reacción de Wagner	+
Reacción de Sonneschein	+
Reacción de Popoff	+
Taninos	+++
Fenoles	+++
Saponinas	-
Lactonas sesquiterpénica	+
Flavonoides	+++

(-) no se observa presencia del Metabolito, (+) baja evidencia, (++) evidencia, (+++) alta evidencia

Tabla 2. Cuantificación de metabolitos secundarios presentes en el extracto etanólico de la cáscaras de *Annona muricata* L.

Ensayos de cuantificación	Extracto etanólico de cáscaras de <i>Annona muricata</i> L.
Alcaloides (% lupanina)	2,0530
Flavonoides (mg quercetina/mL)	0,1545

La presencia de sistemas aromáticos con heteroátomos de N y O en el extracto etanólico de la cáscara de *Annona muricata* L. pueden contribuir sinérgicamente entre ellas en la protección contra la corrosión del acero en medio ácido debido a la adsorción de las moléculas del inhibidor en la superficie del acero [7,12,13,20-22].

3.2 Ensayos gravimétricos

Los estudios realizados por pérdida de peso del acero SAE 1008 en HCl 0,5M se realizaron en ausencia y en presencia del inhibidor obtenido del extracto etanólico de cáscaras de *Annona muricata* L. a diferentes concentraciones, del 1% al 6% v/v, para un tiempo de inmersión de 2h a temperatura ambiente. Los parámetros de corrosión obtenidos por los ensayos gravimétricos son mostrados en la Figura 1 y en la Tabla 3.

Con el incremento de la concentración del extracto etanólico de cáscaras de *Annona muricata* L., la velocidad de corrosión disminuye mientras que la eficiencia aumenta con el incremento de la concentración del extracto inhibidor del 78,8% al 91,4%. Del 1% al 2% v/v la eficiencia aumenta significativamente mientras que del 2% al 6% v/v lo hace menos significativamente. La mayor eficiencia de inhibición fue alcanzada al 6% v/v.

Tabla 3. Parámetros de corrosión obtenidos a partir de la pérdida de masa del acero en HCl 0,5M a diferentes concentraciones del extracto inhibidor.

Conc. de extracto (%v/v)	V_{corr} (mpy)	Eficiencia de la inhibición η (%)	Superficie cubierta Θ
BLANCO	132,29	---	---
1	27,99	78,8	0,79
2	18,36	86,1	0,86
3	15,26	88,5	0,88
4	14,28	89,2	0,89
6	11,38	91,4	0,91

3.3 Curvas de polarización

En la Figura 2 se muestra las curvas de polarización del acero SAE 1008 en solución de HCl 0,5M en ausencia y presencia del extracto etanólico inhibidor a diferentes concentraciones del inhibidor a temperatura ambiente. Los parámetros cinéticos obtenidos a partir de las curvas de polarización potenciodinámica por el método de extrapolación de Tafel se presentan en la Tabla 4. Los valores de R_p obtenidos a partir de la resistencia a la polarización lineal así como la eficiencia de inhibición, η (%), obtenida a partir de los valores de la densidad de corriente de corrosión (i_{corr}) también se muestra en la Tabla 4.

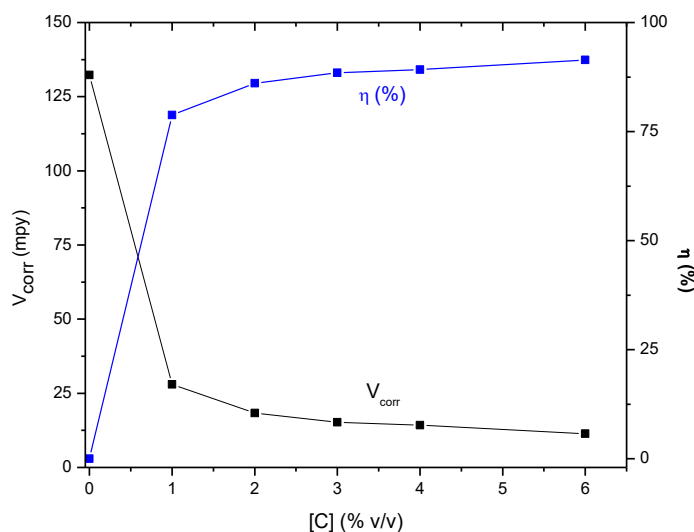


Figura 1. Dependencia de la velocidad de corrosión y la eficiencia de inhibición, η (%) con la concentración del extracto etanólico de cáscaras de *Annona muricata* L. sobre el acero SAE 1008 en HCl 0,5M a temperatura ambiente.

En las curvas de polarización anódica y catódica mostradas en la Figura 2, se puede observar que el incremento de la concentración del extracto inhibidor en la solución ácida, afecta ambas reacciones, anódica y catódica, producidas en la superficie del acero determinando un E_{corr} más negativo que la superficie no inhibida. Estas curvas de polarización muestran que la disolución anódica del acero se reduce y al mismo tiempo, la reacción catódica de evolución de hidrógeno, es retardada probablemente debido al bloqueo superficial que se produce debido a la adsorción de las moléculas del extracto inhibidor sobre la superficie del acero [18-20].

La presencia del extracto inhibidor reduce la velocidad de corrosión del acero sin modificar significativamente el aspecto de la curva de polarización respecto a aquella que no contiene el inhibidor. A partir de los resultados reportados en la Tabla 4, se puede establecer que los valores de E_{corr} del acero en HCl 0,5M en presencia del extracto inhibidor respecto a E_{corr} en ausencia del mismo, varían hacia la dirección más negativa con el incremento de la concentración del extracto inhibidor, alcanzando variaciones entre 22 - 34 mV; sin embargo, no se puede establecer una relación directamente proporcional entre el E_{corr} y el incremento de la concentración del inhibidor.

Tomando en cuenta que para la clasificación de un inhibidor [21], cuando la diferencia entre el E_{corr} en presencia y ausencia del inhibidor es mayor de 85 mV se le puede clasificar como inhibidor anódico o catódico, se puede establecer que el extracto inhibidor en estudio es del tipo mixto.

La densidad de corriente de corrosión (i_{corr}) disminuye apreciablemente con el incremento de la concentración del inhibidor probablemente debido al incremento en el porcentaje de área superficial bloqueada por la adsorción del inhibidor. Las pendientes β_a y β_c muestran también una variación con el incremento en la concentración del inhibidor, aunque la pendiente catódica se ve mucho más afectada que la anódica, con lo cual se presume de un mixto con características predominantemente catódica. La resistencia a la polarización (R_p) también se incrementa considerablemente con el aumento de la concentración del extracto inhibidor. De la eficiencia de inhibición calculada a partir de la densidad de corriente (Ecuación (4)) se tiene que la eficiencia aumenta con el incremento de la concentración del extracto inhibidor alcanzando un valor máximo de 91% al 6%v/v.

Los valores de eficiencia de inhibición obtenidos a partir de las curvas de polarización y reportados en la Tabla 4, muestran similar tendencia que los obtenidos en los ensayos gravimétricos.

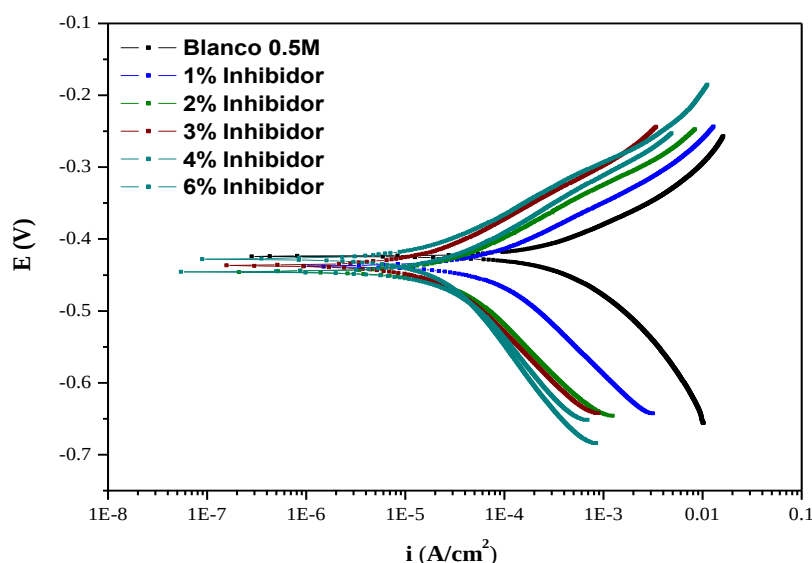


Figura 2. Curvas de polarización potenciodinámica del acero en HCl 0,5M en ausencia y presencia.

Tabla 4. Parámetros de la polarización potenciodinámica del acero en HCl 0,5M a diferentes concentraciones del extracto inhibidor.

Conc. de extracto %v/v	E_{corr} mV (SCE)	i_{corr} $\mu A/cm^2$	Pendientes de Tafel (mV/década)		R_p $\Omega \cdot cm^2$	η (%)
			β_a	β_c		
BLANCO (HCl 0,5M)	-415	225,50	66,2	-65,6	34,68	---
1	-438	59,30	71,9	-95,7	289,54	73,7
2	-446	26,00	77,4	-114,6	738,92	88,4
3	-437	25,06	77,8	-119,6	773,60	88,9
4	-446	23,60	83,7	-127,3	894,24	89,5
6	-449	18,56	92,6	-126,6	1204,89	91,8

3.4 Isoterma de adsorción

El uso de isotermas de adsorción en el estudio de la capacidad de inhibición de la corrosión de un inhibidor, es una herramienta muy usada para inferir sobre su mecanismo de inhibición. El tipo de isoterma de adsorción aporta información relevante sobre las propiedades de los componentes presentes en el extracto inhibidor. La capacidad de adsorción depende de la composición química, potencial, temperatura, etc. [22]. Los valores de superficie cubierta (Θ) a diferentes concentraciones del inhibidor son reportados en la Tabla 3. Según la isoterma de adsorción de Langmuir, Θ está relacionada con la constante de equilibrio de adsorción (K_{ads}) y la concentración (C) del inhibidor por la ecuación:

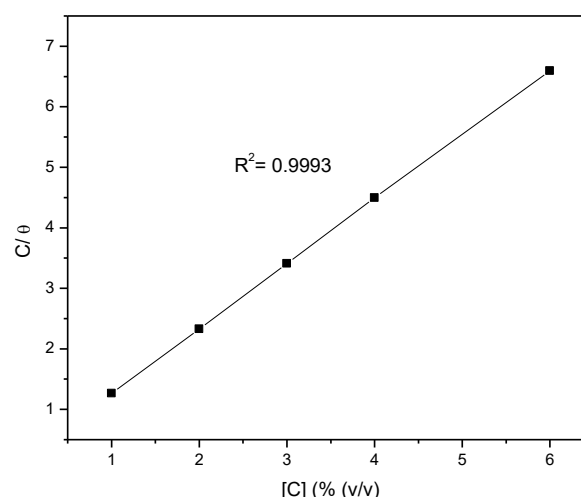
$$C/\Theta = 1/K_{ads} + C \quad (5)$$

La Figura 3 muestra la relación de C/Θ a diferentes concentraciones del extracto inhibidor, C , la cual da una línea recta con pendiente próxima a la unidad para las diferentes concentraciones del extracto inhibidor, sugiriendo que la adsorción del inhibidor a diferentes concentraciones está gobernada por la isoterma de adsorción de Langmuir con un valor de K_{ads} , de 18,52 L/g.

3.5 Morfología superficial

La Figura 4 muestra las imágenes de MEB de la superficie del acero SAE 1008 expuestas en HCl 0,5M en ausencia y en presencia de los extractos etanólicos de las cáscaras de *Annona muricata* L. Las imágenes de MEB muestran la reducción del deterioro superficial que experimentaron las muestras de acero en presencia del extracto,

confirmando la capacidad inhibidora de la corrosión de estos extractos frente al medio agresivo, el cual produjo un severo ataque del acero, evidenciado por una corrosión generalizada de aspecto rugoso en ausencia del inhibidor, ver Figura 4.

**Figura 3.** Isoterma de Langmuir para la adsorción de diferentes concentraciones del extracto etanólico de cáscaras de *Annona muricata* L. sobre el acero SAE 1008 en HCl 0,5M a temperatura ambiente.

4. CONCLUSIONES

El extracto etanólico de las cáscaras de *Annona muricata* L. presenta propiedades inhibidoras de la corrosión del acero en medio ácido, HCl 0,5M. Las curvas de polarización del extracto inhibidor indican que es un inhibidor del tipo mixto con características predominantemente catódico y que su eficiencia de inhibición aumenta con el incremento

de la concentración del extracto inhibidor alcanzando una eficiencia de 91% cuando la concentración es del 6% v/v lo cual guarda relación con los resultados obtenidos por pérdida de masa. La relación que se produce entre el área cubierta de metal con la concentración del inhibidor obedece a una isoterma de Langmuir, la cual describe que el área cubierta de metal por adsorción del inhibidor aumenta con el incremento de la concentración del inhibidor y que dicha adsorción es espontánea. La capacidad de inhibición de la corrosión del acero en medio ácido por acción del extracto inhibidor quedó evidenciada por las imágenes de MEB del acero, el cual redujo significativamente su ataque superficial.

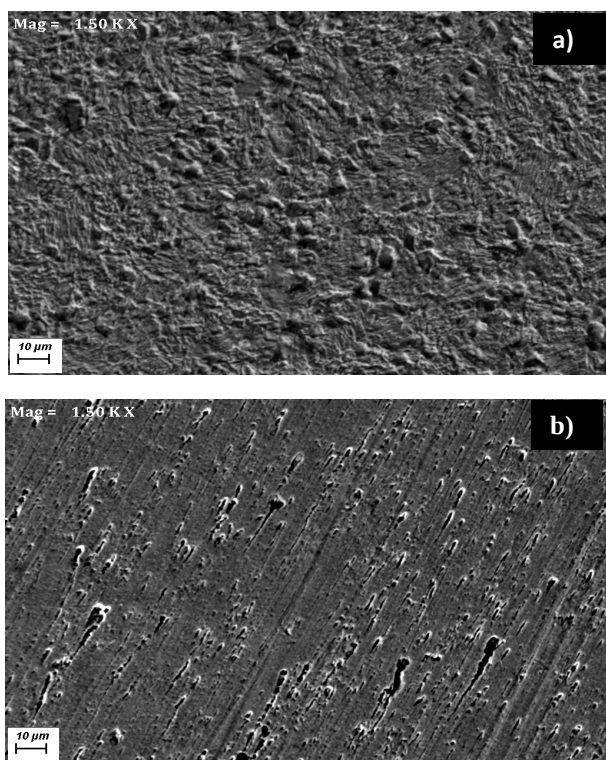


Figura 4. Imágenes de MEB del acero SAE 1008 en HCl 0,5M del ensayo de pérdida de peso, a) sin inhibidor y b) 6,0% v/v del extracto inhibidor de las cáscaras de *Annona muricata* L.

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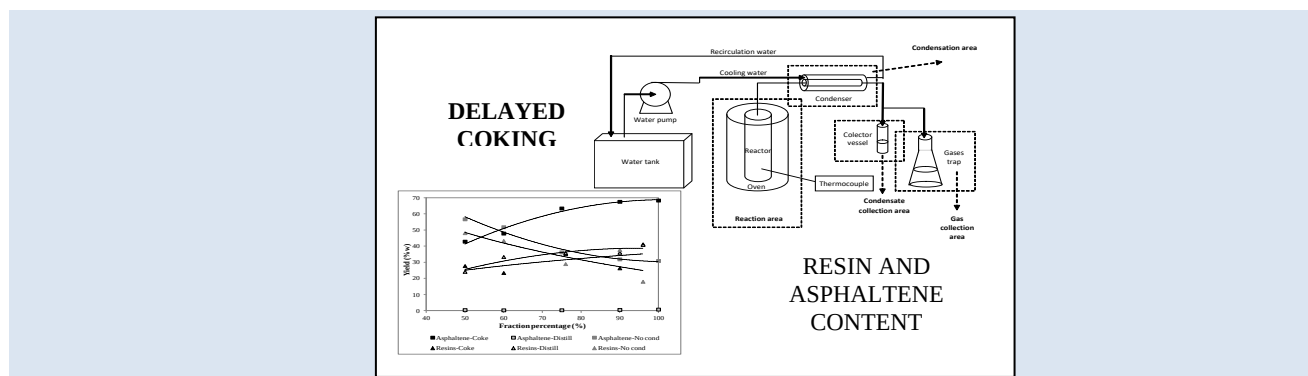
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EFFECT OF RESIN AND ASPHALTENE CONTENT PRESENT ON THE VACUUM RESIDUE ON THE YIELD OF DELAYED COKING PRODUCTS

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ABSTRACT

The effect of resin and asphaltene concentration in the feed, on the yield of delayed coking products was assessed, feeding controlled concentrations of the groups: saturates, aromatics, resins and asphaltenes (SARA) (50-100%w/w of asphaltene or resin and a fixed mass ratio of the others groups) prepared from a Venezuelan vacuum residue. The results of yield of products obtained in a laboratory-scale process show, that the increases of concentration of resins or asphaltenes raise yield of coke and decreases the not-condensable. The distillates yield remained at levels close to zero (<1%w/w) when asphaltene rich blends were fed, while in case of resin rich blends, the amount of distillate produced increased when the resins contents increased. These results are consequence of a higher condensation level of the molecules present in the crude. For distillates, a discriminatory behaviour occurred depending on in which fraction was rich the blend fed to the process, with yields in the order of 20-40% w/w for the mixtures rich in resins and practically equal to zero in the case of mixtures rich in asphaltenes.

Keywords: Resin, Asphaltene, Vacuum residue, Delayed Coking.

EFECTO DEL CONTENIDO DE RESINAS Y ASFALTENOS PRESENTE EN EL RESIDUO DE VACIO SOBRE EL RENDIMIENTO DE LOS PRODUCTOS DE LA COQUIZACIÓN RETARDADA

RESUMEN

Se evaluó el efecto de la concentración de resinas y asfaltenos en la alimentación sobre el rendimiento de los productos de la coquización retardada, a partir de la alimentación de mezclas de composición controlada de los grupos SARA: saturados, aromáticos, resinas y asfaltenos (50-100%p/p de resinas o asfaltenos y una relación másica fija entre los restantes grupos) que fueron preparadas usando como base un residuo de vacío venezolano. Los resultados del rendimiento de los productos, obtenidos en un proceso a escala laboratorio muestran que, el aumento en la concentración de las resinas o de los asfaltenos incrementa el rendimiento de coque y reduce el de los no-condensables. En cambio, el rendimiento de los destilados permanece en niveles cercanos a cero (<1%p/p) cuando se alimentan mezclas ricas en asfaltenos, y se incrementa cuando se alimentan mezclas ricas en resinas. Estos resultados son consecuencia del alto nivel de condensación de las moléculas presentes en el crudo. En el caso de los destilados, se observó un comportamiento discriminatorio dependiendo de cuál era la fracción mayoritaria en la mezcla alimentada al proceso, con rendimientos del orden de 20-40%p/p para las mezclas ricas en resinas y prácticamente iguales a cero en el caso de las mezclas ricas en asfaltenos.

Palabras claves: Resinas, Asfaltenos, Residuo de vacío, Coquización Retardada.

1. INTRODUCTION

There are different types of treatments for heavy and extra heavy crude, being delayed coking one of the most widely used methods in Venezuela. The delayed coking process feeds itself mainly from vacuum residue, which is thermally treated so as to have two types of endothermic reactions occur, ones from cracking in order to obtain liquid and gas products and, others from polymerization-condensation where coke is obtained as a solid product [1].

This technology has been investigated since the 1950s, with the greatest amount of contributions in the 1970-1990s. In spite of this is a proven technology and the belief that new things cannot be obtained from it, authors like [2, 3, 4] look for to rescue the key role of this technology within the processes of refining, especially nowadays, when streams with a higher content of heavy fractions are being processed by the refineries worldwide.

In recent years, some works have been developed in the search to deepen into what happens within the coking process, since despite numerous investigations developed, not everything has been clear. Simulations [5, 6], proposals for kinetic models [7, 8, 9, 10] and prediction of yields of the products obtained [11, 12], try to establish those theoretical aspects that have not yet been elucidated.

In addition new trends on the use of other technologies to achieve improvements in the coking process have appeared, such as the use of additives [13], nanocatalysts [14] and the integration of processes or combined technologies that seek to take advantage of each one in order to obtain improvements in performance as in characteristics of the obtained products. The union of delayed coking with technologies such as [15]: deasphalting, gasification, ebullated bed, slurry phase hydrotreating, ultrasonic-assisted method [16] has shown to be beneficial for both, performance and the desired characteristics of the final products.

In the specific area of behavior of the key variables, works such as [17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29] show the influence of these on the yield and characteristics of the products obtained, for these new heavy and extra-heavy crudes that are being extracted from the subsoil in those countries such as the Venezuelan case, whose crude reserves have API gravities lower than the obtained in recent

decades.

In previous works [23, 24], it was established the necessity of study the impact of crude oil constituent SARA fractions by separated, over the yield and the characteristics of products of delayed coking in general and in special for Venezuelan case, due to the narrow range of feed compositions that was studied in past [25, 26, 27, 28, 29], extending the evaluation range of the presence for each fraction in the feed [24].

From a laboratory scale study of delayed coking [23, 24] employing vacuum residues designed and constructed from heavy and extra heavy Venezuelan crude oils (with a high asphaltene proportion), it was evaluated the influence of the content and proportion of the SARA fractions and other basic characteristics like: volatile material, sulfur or heavy metals content, over the yield and quality of obtained products (coke, liquid and non-condensable). This constructed feeds that were rich in one of the hydrocarbon characteristic groups SARA, were prepared from three Venezuelan vacuum residues identified in based their origin as: Petrozuata, Amuay and Cardon, by means of the separation of their SARA fraction constituents, which were mixed maintained a controlled composition and higher to 50%w/w of each one of SARA fractions, generating the feeds denominated base-residuals.

These base-residuals were characterized in based on the C/H relation, immediate analysis, concentrations of heavy metals and Conradson Carbon, being that for those containing high concentrations of saturated and aromatic groups, C/H relation was lower, volatile material was greater, and the concentration of heavy metals and Conradson carbon were lower than in the case of residuum with higher concentrations of resin and asphaltene groups. Also it was obtained that the possibility of cracking and coke formation of the residuum, is directly related to the presence of the latter two groups in the crude oil [23]. Then, when the feeds were introduced in the coking process, the results show that an increment in yield of coke and gases, and a diminishing in yield of liquids, is obtained when the resins and asphaltenes concentration is incremented or aromatics and saturates concentration diminished. With regard to physicochemical analysis, it was observed that in all cases, the measured variables (C/H, metals, and sulfur content) change in an

important way with increasing the presence of more polar and heavy fractions. The results correspond to the expected theoretical trends and show that each constituent group has a markedly different effect in the products obtained in the process [24].

These works [23, 24], although permit to evaluate the influence of the SARA groups from controlled composition feeds, did not achieve to evaluated the whole range of composition (intermediate values), reason why it was proposed to extract from a determined vacuum residue the constituent fractions and to extend the range of evaluation for the three more important group presents in the Venezuelan characteristic crude oil: aromatic, resin and asphaltene. The obtained results in the case of aromatics can be review in [30].

The general objective of this research was to evaluate the effect of the composition of resins and asphaltenes in the feed to the delayed coking process on the yield of the products, using a laboratory .scale. In order to fulfill this objective work was used an vacuum residue known as Merey. Merey is heavy crude of 16° API from Eastern Venezuela and from which ten blends were prepared: five rich in resin fractions and five rich in asphaltenes, to later on assess and relate the effect of this composition with the product yield obtained from the delayed coking process. The coking was carried out in a delayed coking unit at laboratory scale at the Carbon and Oil Residue Laboratory at Simon Bolivar University. In addition, the prepared blends were analyzed by means of Infrared Spectroscopy (IR) to identify the functional groups present and the existing differences in the intensity of the signals as a function of resins and asphaltenes presence.

This research intends to suggest improvements to the delayed coking process using Venezuelan crude and it aims to assess a profile of the resins and asphaltenes composition that will enable identifying the existing tendency between the composition of such fractions in the feed and yield of the products, this can be used by refinery planning units when making decisions in the selection of treatment strategies when the expected feeds have a high content of resins or asphaltenes.

2. METHODOLOGY

2.1 Residue separation in Saturates, Aromatics, Resins and Asphaltenes (SARA)

An SARA analysis was performed on the Merey vacuum residue following the ASTM D4124-09 norm [31] to identify its composition.

Afterwards, an SARA separation was done from the same residue by means of a greater scale method. Such separation was made aimed at obtaining enough quantity from every fraction of hydrocarbons that would enable for the preparation of blends with different percentages in weight of the SARA groups that will feed the delayed coking process.

The procedure to conduct the SARA separation from the Merey residue follows the methodology exhibited by [32]. For the precipitation of the asphaltenes, the method used by [33] was applied, using n-hexane as solvent, the residue was mixed with n-hexane in a 1:30 proportion, and the put into an agitation plate, to mix them for 6hrs, after which was filtered to separate the solid (asphaltene) and the liquid fraction (part of the maltenes). The solid fraction is washed in a soxhlet with n-hexane until the solvent was clear. The liquid remaining in the bottom was mixed with the before liquid fraction to conform the maltenes fraction, which was submitted to distillation to separate it from the solvent.

The maltene separation technique is a variation of the norm ASTM D4124-09 [31] and of the methodology developed by [34]. This norm (ASTM D4124-09) was selected because the similarity in characteristics, between heavy residue and asphalt. The method employed is based on the same adsorption and affinity principle with the solvents used in the norm ASTM D4124-09 [31], but 4 balloons are used as substitutes of the adsorption column, among which 25 g of alumina and silica gel were equally distributed, grade chromatographic, per maltene gram [23, 34], alumina in the first two balloons and silica gel in the last two were distributed.

The liquid obtained in the asphaltene separation after distillation, was mixed with n-hexane (1:150) and a portion of it was collocated in the first balloon shaking it for 2 min and leaving it in rest for 10 min. Then the supernatant was transferred to the next balloon, and put into the first balloon a new portion of the mix. Both balloons were then shaken for 2

min and leaving them in rest for 10 min. And so on with the rest of balloons until all the total mix maltene-n-hexane was transferred. The remaining liquid in the last balloon was reserved to separate after, the saturates fraction. This procedure was repeated with toluene (1:120) and a mixture 1:1 of toluene/methanol (1:120) to obtain the aromatic and resin fraction respectively. The remaining liquids in the three cases were collocated in a rotoevaporator to separate the three desired fractions from the solvents employed. An SARA analysis was done to the fractions obtained: asphaltene, first fraction obtained with n-hexane, second fraction obtained with toluene and third fraction obtained with toluene/methanol, according to the norm ASTM D4124-09 [31] to determine if they indeed correspond to saturates, aromatics, resins and asphaltenes.

2.2 Preparation for the delayed coking feeding process

The design of the mixtures consisted in construct 5 blends with a high content of resins and 5 with high content of asphaltenes, specifically between 50-100%w/w. The proportion between the remaining fractions was established as follow: in resin blends, 10%w/w of saturate fraction, 45%w/w of aromatic

and asphaltene fractions; in asphaltene blends, 10%w/w of saturate fraction and 45%w/w of aromatic and resin fractions. This is for example, in a resin rich blend with 50%w/w of resin, the remaining 50%w/w correspond to 5%w/w of saturate fraction (10%w/w of the rest), and 22.5%w/w for aromatic and asphaltene fraction respectively (45%w/w of the rest). This design looked for maintain controlled relationship between the remaining fractions, but because it was not possible to obtain pure fractions (as it is shown later) the proposed blends were not achieved and the resulting blends are presented in table 1.

For the feeding process of delayed coking ten blends were prepared: five with high resin content and five with high asphaltene content. In the five blends with a resin representative composition, such fraction composition was varied between 50 and 96 %w/w, (see Table 1). Is range was used due to the fact that the recovery of the fractions did not enable the obtaining of more than 96 %w/w of resins. For the preparation of such blends, the third fraction obtained with toluene/methanol was used as a basis to adjust the resins content and, in addition, a constant relation was maintained between the aromatics and asphaltenes content.

Table 1. Prepared blends for the delayed coking process.

Sample	Saturates(%w/w) $\pm \sigma$	Aromatics(%w/w) $\pm \sigma$	Resins(%w/w) $\pm \sigma$	Asphaltenes %w/w) $\pm \sigma$
1	21 $\pm$ 1	8 $\pm$ 1	50 $\pm$ 1	21.0 $\pm$ 0.1
2	17 $\pm$ 1	7 $\pm$ 1	60 $\pm$ 1	17.0 $\pm$ 0.1
3	9 $\pm$ 1	5 $\pm$ 1	76 $\pm$ 3	9.0 $\pm$ 0.1
4	4 $\pm$ 1	2 $\pm$ 1	90 $\pm$ 1	4.0 $\pm$ 0.1
5	2 $\pm$ 1	2 $\pm$ 1	96 $\pm$ 1	0.0 $\pm$ 0.1
6	21 $\pm$ 2	8 $\pm$ 1	21 $\pm$ 3	50.0 $\pm$ 0.1
7	17 $\pm$ 2	6 $\pm$ 1	21 $\pm$ 3	60.0 $\pm$ 0.1
8	11 $\pm$ 2	4 $\pm$ 1	11 $\pm$ 3	75.0 $\pm$ 0.1
9	4 $\pm$ 2	2 $\pm$ 1	4 $\pm$ 3	90.0 $\pm$ 0.1
10	0 $\pm$ 0	0 $\pm$ 0	0 $\pm$ 0	100.0 $\pm$ 0.1

However, for the blend of 96 %w/w of resins it was not possible to adjust such a relation since any other arrangement among the fractions obtained made the resins content decrease to a percentage below 96 %w/w.

For the five blends with a representative

composition of asphaltenes, the composition of this fraction was varied between 50 and 100 %w/w, (see Table 1) (σ represents the standard deviation of the experimental values). For the preparation of such blends, the fraction obtained forms the asphaltene precipitation was used as the basis to adjust the

asphaltene content and, a approximated constant relation between aromatics and resins content was maintained.

To guarantee homogeneity of the prepared blends, these were subject to a heating-shaking process with approximately 20 ml of toluene, slowly incorporating the corresponding quantity of each fraction. Once the sample is homogenized, the toluene was extracted based on the volatility difference.

Once the composition of the fractions at a greater scale was identified by mass balance, the mass required from each fraction was calculated to prepare the blends according with Table 1.

2.3 Delayed coking process at laboratory scale

The delayed coking was conducted in a laboratory scale unit located in the Carbon and Petroleum Residue Laboratory at Simon Bolivar University (see Figure 1) described in detail by [35].

Coking was conducted in a 0.7 x 12 cm, vertical reactor, presenting minor dimensions in comparison with the reactor used by Meza-Avila and collaborators [23], to try to reduce the drag of liquid fractions presented during the tests in the previous works [23, 24].

The operating conditions of the laboratory unit that were studied by [23, 24, 27, 28] were fixed to investigate only the feed composition effect. Employing a load of 2g, the variables used were: temperature 650 °C, reaction time 60 min, heating rate 5 °C/ min and 150 ml/ min of nitrogen as carrier gas. These operational conditions remained fixed for the thermal treatment of each blend. The start-up of the delayed coking unit was conducted as per the steps presented by [36].

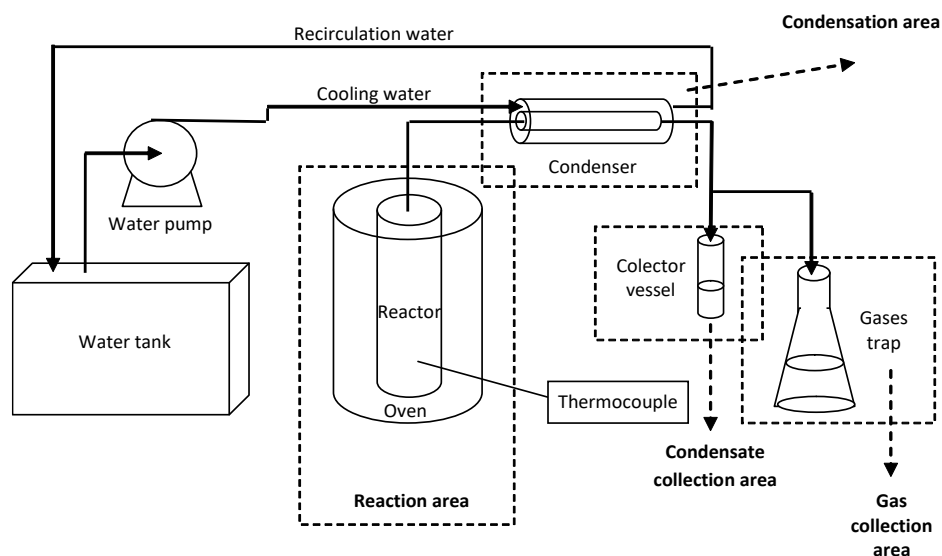


Figure 1. Delayed coking unit at laboratory scale [24].

2.4 Feeding Characterization to the delayed coking process

The fractions obtained from the SARA separation were subjected to the SARA analysis conducted at a greater scale through the Norm ASTM D4124-09 [31]. And the prepared blends were submitted to a functional groups identification by means of Infrared Spectroscopy (IR) using the ThermoNicolet iS5 iD5 ATR.

3. RESULTS AND DISCUSSION

3.1 Residue separation in Saturates, Aromatics, Resins and Asphaltenes (SARA)

Following the norm ASTM D4124-09 [31] and as of the SARA analysis of the Merey residue vacuum, 6.88 %w/w saturates, 23.32 %w/w aromatics, 46.22 %w/w resins and 23.57 %w/w asphaltenes were obtained [37, 38].

To conduct SARA separation at a greater scale of the Merey residue vacuum, the procedure proposed by [32] was used. A 23 %w/w percentage recovery was obtained for the asphaltene fraction. For the maltene separation the methodology was applied guaranteeing that the adsorbents were to be used immediately if their activation process was concluded. In Table 2 the recovery percentages of the maltene fractions obtained are shown.

Table 2. Fraction recovery from maltenes.

<i>Fraction</i>	<i>Recovery (%w/w) $\pm \sigma$</i>
First fraction	24.0 $\pm$ 0.9
Second fraction	26 $\pm$ 2
Third fraction	50 $\pm$ 2

Once the fractions were obtained, an analytical SARA was conducted to know their composition and so minimize the error at the moment of preparing the blends to feed in the delayed coking process (See Table 3). It can be observed in Table 3 that an aromatic drag was obtained at the first fraction obtained with n-hexane and a resin drag at the second fraction obtained with toluene. These deviations in the maltene separations presented themselves due to a greater scale proceeding that does not enable maintaining the same relations between the alumina and the silica with the maltene grams used. Upon conducting the SARA analysis of each fraction following the norm ASTM D4124-09 [31], it was noted that the proportion between the alumina and the silica gel gram per maltene gram is around 500.

Table 3. SARA analysis results of the separated fractions.

<i>Fraction</i>	<i>Saturates (%w/w) $\pm \sigma$</i>	<i>Aromatics (%w/w) $\pm \sigma$</i>	<i>Resins (%w/w) $\pm \sigma$</i>	<i>Asphaltenes (%w/w) $\pm \sigma$</i>
First fraction	48.8 $\pm$ 0.4	45.3 $\pm$ 0.6	5.9 $\pm$ 0.5	0 $\pm$ 0
Second fraction	0.64 $\pm$ 0.07	84 $\pm$ 2	16 $\pm$ 1	0 $\pm$ 0
Third fraction	1.5 $\pm$ 0.2	3.0 $\pm$ 0.5	95.5 $\pm$ 0.9	0 $\pm$ 0

3.2 Delayed coking process at laboratory scale

Once the blends were prepared as it was explained before, they were introduced to the delayed coking process in laboratory scale. Figure 2 shows the yields obtained for the five prepared blends with a high resins and asphaltenes content respectively. The results are expressed for the coke, as well as the distilled and non- condensable products.

Figure 2 shows at a general level that the coke yield increased as the resins composition increased in the feeding of delayed coking process, a behaviour that was maintained for the distillates yield. On the other hand, the yield in non-condensable products decreased with the increase of resins composition in the blends.

For blends with a high content of asphaltenes, Figure 2 shows a more important increase of the yield in coke with the increase in composition of this hydrocarbon feeding fraction. For this group of blends, as the asphaltene content increased, a non-significant yield in distillates and a decrease in the yield of non-condensable products were obtained.

It was also possible to identify that the coke yield obtained for blends with a high content of

asphaltenes resulted greater than that of the blends with high resin content, the same as that of the yield of non-condensable products.

These results correspond with the reported in previous studies, from where it was confirmed that the coke yield increases as the heavier fractions content increases (resins and/or asphaltenes) being the asphaltene content the most important for the coke formation, follows of the resins content [24, 39, 40].

Both fractions are mainly poly-aromatic hydrocarbons with aliphatic side chains that due to heat, break up or crack producing aromatic free radicals or poly aromatics of a smaller size, which can generate re-arrangements or molecular re-combinations by condensation producing hydrocarbons with poly-aromatic structures of greater weight and molecular size (poly-condensing), which are the preceding ones for coke formation [41]. Therefore, as their content increases at feeding, the greater the condensation will be among the poly-aromatic structures present, giving rise to the formation of a greater quantity of poly-condensing structures and encouraging coke

formation.

In addition, a greater yield in gases and a minor one for the liquid products was obtained with the increase in the asphaltene content and an inverse behaviour for the case of resins content increase. This result shows that the asphaltenes preferably take the way of a greater intensity cracking of the outermost fractions which give rise to compounds of low molecular weight comprising the non-condensable products, followed by complete

condensation reactions which give rise to a high coke proportion [42], while in the case of resins, the low-intensity cracking reactions generated by smaller molecules and the partial condensation reactions, from which the generated low-boiling aromatic compounds recombine causing a higher proportion of liquids and coke in the process, appear to be favoured in similar proportions [42].

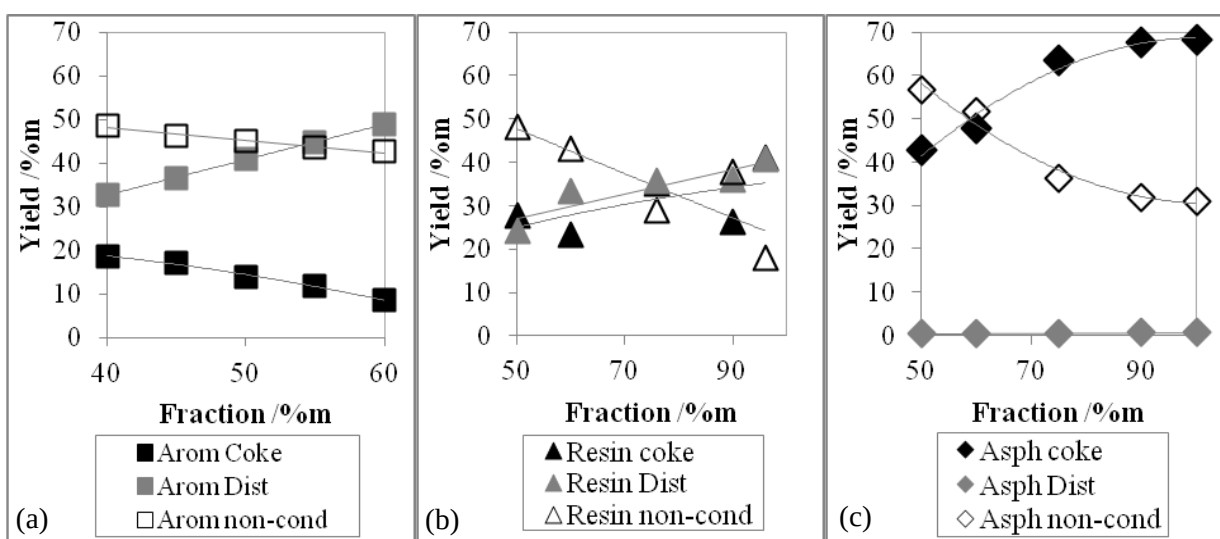


Figure 2. Yield of the delayed coking products for the prepared blends: a) Aromatics, b) Resins, c) Asphaltenes.

3.3 Feeding characterization to the delayed coking process

The method IR was conducted for 5 blends prepared with a high resins and asphaltene content. The spectra obtained were compared among each other to identify the present functional groups of resins and asphaltenes through the signals registered associated to these groups and the existing differences in the intensity depending on their composition in the blends. Figure 3 shows the spectra obtained for the extreme points of each group of blend.

From Figure 3 it can be observed that in all cases the same signals were obtained in the same ranges of wave numbers, which indicates the presence of the same functional groups for the blends rich in resins and asphaltenes correspondingly. For the blends with a high resins content it was noted that the spectra did not present representative differences due to the fact that the signals of blends with 50 and

96 %w/w overlap; however, there was a slight decrease (2-3%) in the wave intensity at 2923, 2852, 1456 and 1376 cm^{-1} with the increase in resin composition, which points at a minor presence of simple links due to more condensed blends with a higher resins content and a smaller content of saturates and aromatics.

Likewise, it was noted that for the rest of the signals (1700, 1600, 1020, 886, 812, 746 and 722 cm^{-1}) there was a slight increase (3-4%) in the intensity with the increase of the resins composition, which confirms a smaller presence of simple links and indicates a greater presence of links C=O, C=C, S=O and aromatic condensations for such blends.

For the blends with high asphaltene content, greater differences between the intensity of spectra signals were identified (figures C and D). In this case, as the asphaltene composition increased and the one for the saturates, aromatics and resins decreased, there was a decrease in the intensity of signals to 2923,

2852, 1456, 1376 cm^{-1} , indicating a smaller presence of simple links. In regards to the rest of the signals there was also a slight decrease (2-3%) in the intensity of the signals. The obtained trend can be attributed to the complexity of such a fraction, which is more representative in the sample with 100 %w/w of asphaltenes; therefore, the arrangement, the distribution and in general, the contribution of

this fraction together with the lower content of the rest of the fractions (S.A.R.), could have produced this small decrease in the signals as of 1700 cm^{-1} .

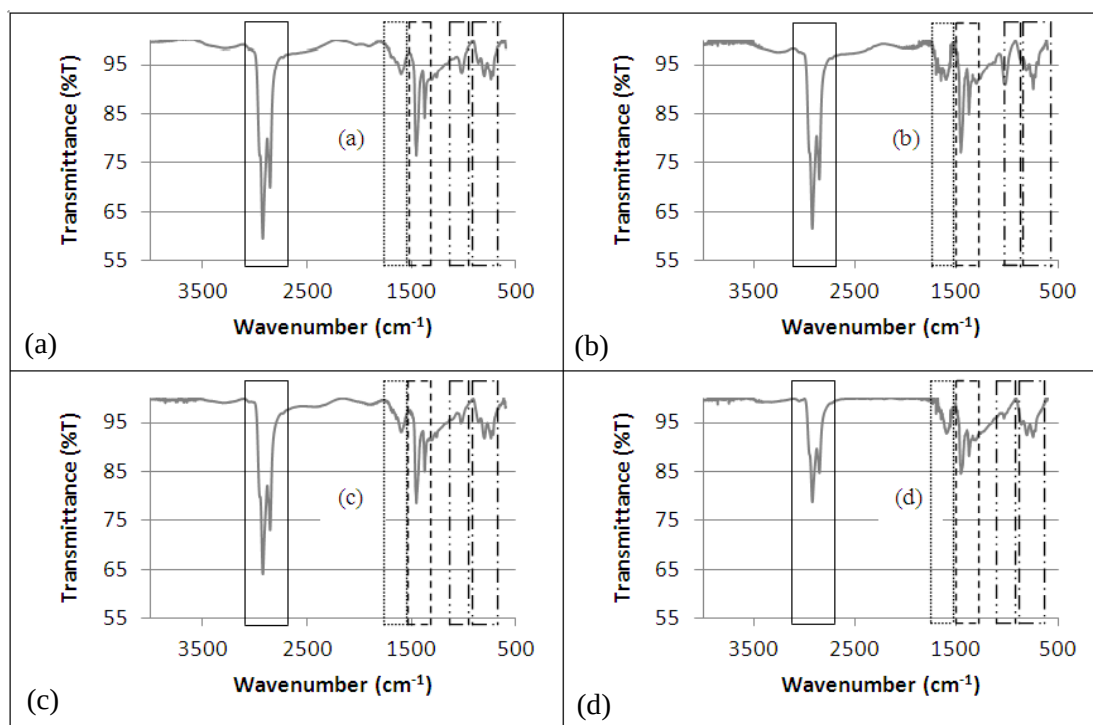


Figure 3. Infrared spectroscopy of the blends: (a) 50 %w resins, (b) 96 %w resins, (c) 50 %w asphaltenes, (d) 100 %w asphaltenes.

On comparing the spectra of the blends rich in resins and asphaltenes, in general it could be observed that for the blends with a greater content of resins a greater intensity was obtained for the signals 2923, 2852, 1456 and 1376 cm^{-1} , while with the analysis of the signals to 1700, 1600, 1020, and of 886 up to 722 cm^{-1} , it could be observed that such signals increase with the presence of a greater resins and asphaltenes content in the prepared blend, which indicates a greater presence of links C=O, C=C, S=O and aromatic condensations respectively.

Such trends were expected because as the blend is more condensed and has more complex fractions as resins and asphaltenes, the contribution of these fractions and their arrangement with the other fractions, makes the presence of simple links decrease as an increase in the presence of benzene

rings, aromatics and heteroatom's condensations, which can influence directly in the yield and characteristics of the delayed coking products.

4. CONCLUSIONS

The study conducted enabled to identify that as the resin composition increases in the feeding to the delayed coking process, the coke and the distilled products yield increases. With the increase in the asphaltene composition a greater yield in coke is generated and a non-significant yield for distilled products, so that the increase of the asphaltene composition weighs negatively in the processes of thermal conversion, mainly due to the conversion yield to distillate products.

It is relevant to highlight this very low production of distillate of asphaltene rich blends that might

suggest that the asphaltenes have a high preference to polymerization allowing only the outermost fractions of the molecule can be cracked to compounds of low molecular weight, which leave the process as not-condensable gases, disadvantaging the objective of the delayed coking process. In the case of the resins both reactions, polymerization and cracking, could occur in more similar proportions, giving rise to larger quantities of distillate as a product of the process.

The blends prepared for the delayed coking process showed the same functional groups, indicating a smaller presence in simple links and a greater presence of benzene rings, aromatics and heteroatom's condensations as the resins and asphaltenes composition increases in the blends typical with a high presence of these groups in hydrocarbons.

Experimental tests could be more effective in the reactions selectivity if they were done with a higher relationship between the grams of alumina and silica gel per maltene gram.

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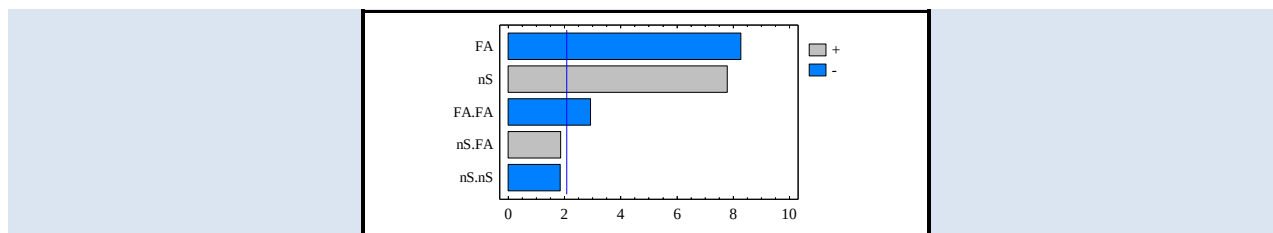
MECHANICAL BEHAVIOR OF QUATERNARY CONCRETE WITH MICRO/NANO SiO_2 ANALYZED BY ARTIFICIAL NEURAL NETWORKS AND SURFACE RESPONSE METHODLuis E Zapata-Orduz^{1*}, Genock Portela², Marcelo Suárez², Brian H. Green³

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ABSTRACT

This paper presents experimental and computational findings related to the compressive strength of concrete containing nano- SiO_2 , fly-ash, silica fume, and polycarboxylate-superplasticizer. At different days of aging, three central-composite experimental designs were performed to assess the role of the input variables. The statistical results indicated linear, interactive, and quadratic effects between the variables as well as mathematical lack-of-fit of the second-order. Hence, artificial neural networks (ANN) with multiple inputs were implemented to assist in understanding the complex nature of the systems. The results indicated that, by using ANN, the compressive strength of the systems could be modeled to improve the concrete's performance acting in conjunction with results obtained from the statistical experimental designs. Sensitivity analyses on the ANN-simulations allowed for quantifying the influence of the multiple input variables and results were physically related to the mathematical lack-of-fit condition inherent in the statistical experimental designs.

Keywords: compressive strength, nano- SiO_2 , silica fume, fly ash, statistical design of experiments, artificial neural networks.

COMPORTAMIENTO MECÁNICO DE MEZCLAS CUATERNARIAS DE CONCRETO CON MICRO/NANO SiO_2 ANALIZADAS EMPLEANDO REDES NEURONALES ARTIFICIALES Y EL MÉTODO DE SUPERFICIE DE RESPUESTA

RESUMEN

Este documento presenta los hallazgos experimentales y computacionales relacionados con la resistencia a la compresión del concreto adicionado con nano- SiO_2 , cenizas volantes, humo de sílice y superplastificante del tipo policarboxilato. Se realizaron tres diseños experimentales centrales compuestos en diferentes días de maduración para evaluar el papel de las variables. Los resultados estadísticos indicaron efectos lineales, interactivos y cuadráticos entre las variables, así como falta de ajuste matemático de segundo orden en los diseños experimentales. Por lo tanto, se implementaron redes neuronales artificiales (ANN) con múltiples variables de entrada para ayudar a comprender la compleja naturaleza de los sistemas. Los resultados indicaron un excelente modelamiento de la resistencia a la compresión de los sistemas y mediante el uso de las ANN actuando en conjunto con los resultados obtenidos de los diseños experimentales se logró mejorar el entendimiento del concreto. Los análisis de sensibilidad en las simulaciones con las ANN permitieron cuantificar la influencia de las múltiples variables de entrada y los resultados se relacionaron con la condición matemática de falta de ajuste y explicaron físicamente con gran éxito los resultados de los diseños estadísticos experimentales que padecían dicha condición.

Palabras Clave: resistencia a la compresión, nano- SiO_2 , micro-sílice, ceniza volante, diseño estadístico de experimentos, redes neuronales artificiales.

1. INTRODUCTION

Increasing employment of nano-modified, high-performance construction materials and systems, such as smart carbon nano-tubes, nano-titania, nano-calcium carbonate, and nano-alumina, is producing materials with higher strength, improved durability, and reduced environmental impact [1]. Specifically, among recent advances in the concrete industry seeking to make concrete more sustainable are the increasing use of binary, ternary, and even quaternary binders [2][3][4]. In effect, such modified cementitious materials result not only in the production of high strength concretes but also in more durable, sustainable, and economical concrete structures [5]. For instance, some years ago, the maximum compressive strength that could be obtained at the construction site was about 40 MPa [6], but today due to recent advancements in concrete technology and chemical and mineral admixtures, concrete with compressive strengths up to 100 MPa are commercially produced [7]. Also, according to the recent research, high strength concrete (HSC) could be considered as a special group of concrete materials due to incorporation of mineral and chemical admixtures so that the compressive strengths exceeds 70 MPa [8]. Nevertheless, in spite of this development in the concrete industry, concretes with compressive strengths of at least 40-60 MPa are still regarded as HSC. In fact, Jajal et al. [9] following the American Concrete Institute Committee ACI 363, defined HSC as the concrete that has a specific compressive strength of at least 41 MPa at 28 days. In this paper, 24 different mix designs with a water-to-binder (w/b) ratio of 0.35 were developed to obtain at least 41 MPa in compressive strength at 28 days by using Portland cement type I, Class F fly ash (FA), silica fume (SF), and nano-SiO₂ (nS) in plain, binary, ternary, and quaternary mixes. The compressive strength was studied at ages of 3, 7, 28, 56, and 90 days, and the analysis of the results were conducted by using both statistical and numerical computer tools, such as design of experiments (DOEs) and artificial neural network (ANN) models, respectively.

ANNs are a powerful tool and are extremely useful in situations for which the rules are either unknown or when response surfaces are highly complex. Hence, the use of ANNs is especially advantageous when traditional predictive mathematical models are

not feasible [10][11][12][13]. However, the flexibility of ANN is linked to one of the most important of their disadvantages, i.e., they are unable to provide explanations and justifications for their answers [10]. In civil engineering, the ANN approach has been widely used to model and analyze a diversity of topics such as: soil behavior [14], torsion in reinforced concrete beams [15], corrosion of the reinforcement [11], recycled aggregates in concrete [12], or connector's strength in steel-concrete composite structures [16]. The effects of ground-granulated blast furnace slag and calcium nitrite-based corrosion inhibitors on the chloride ion permeability and the compressive and tensile strength of concrete specimens have also been adequately modeled using ANN [17]. Koroğlu et al. [18] worked with the flexural capacity of quadrilateral fiber-reinforced polymer confined reinforced concrete columns using both single and combined ANN; the results showed that predictions of the neural simulations were more satisfactory than approaches used currently in the literature. Alshihri et al. [19] satisfactorily modeled the compressive strength of light-weight concrete by using both feed-forward back-propagation and cascade correlation. Madandoust et al. [20] used ANN and adaptive neuro-fuzzy inference to study *in situ* concrete strength by means of cores cut from hardened concrete; the results showed that both methods have great ability for predicting concrete compressive strength. Finally, the split-tensile strength and water permeability of concrete containing Fe₂O₃ nanoparticles was studied by Nazari et al. [21] using ANN and genetic programming. According to their results, both models have strong predicting potential, although ANN exhibited better performance.

The aim of this study is to predict compressive strength of concrete samples containing nS along with SF and/or FA in the presence of SP by using ANN as a tool complementary to a series of DOE at different ages of maturity of the samples. Three different arrays were employed at each age, i.e., DOE I (nS-FA), DOE II (nS-SF), and DOE III (nS-SF-FA). The partition was made in three DOEs keeping in mind that the upper values of each of the variables employed (nS, SF, FA) were developed in the real limits used in field (not only under laboratory conditions). As presented earlier, ANNs have been applied in fields where the development of a theoretical model is not a straightforward task

due to the many parameters involved in the final value of the property being quantified. Consequently, in this research, an ANN approach intends to assist numerical studies on compressive strength based on DOE in order to obtain a better physical understanding of the global behavior of the systems. Contrary to other fields of research where DOE surfaces adjust well [22][23], in cementitious systems sometimes the surfaces exhibit mathematical lack-of-fit (LOF) of the second order [24]. In this investigation, the ANN results were more representative of the surface responses than the results from DOE since the latter exhibited lack-of-fit of the second-order in all of the cases. Consequently, ANN simulations brought forth better understanding of the overall behavior because the evolution through the time of the systems could be captured in a single equation. In addition, the sensitivity analysis conducted on the ANN models helped in understanding the lack-of-fit exhibited by the DOE methodology.

It should be noted that it was not an objective of this paper to develop a comparative study between DOEs and ANNs models. Instead, the goal was to demonstrate the concurrence and complementary roles played by each methodology in evaluating and physically assisting in understanding the complex experimental behaviors found in the concrete sciences. Finally, the novelty in this research consists in mathematical findings by using ANN about the reason why some concrete (cementitious)

experiments or models where DOEs are employed exhibit LOF. Numerous papers are focused on either research in cementitious-ANN or cementitious-DOE, while this research is focused on the complementary benefits for concrete research of each one of this powerful techniques. Specifically, a key reason found in this work about the reason why DOEs exhibited LOF is related to the fact that from ANN sensitivity analysis the nS, SF, and FA inputs were not necessarily the most important contributing variables to compressive strength; but nS, SF and FA are often the only inputs in the mathematical DOE analysis. The major importance of these novel findings lies at the moment of making a decision about the pertinence of the most common variables employed in concrete technology in the DOE analysis and their possible relationship with the undesirable but very often LOF, which is exhibited by the majority of the cementitious systems.

2. MATERIALS AND METHODS

2.1 Materials

2.1.1 Portland Cement

The concrete samples were prepared using Portland cement type I according to ASTM C150 [25]. Table 1 shows the physical, chemical, and mineralogical characteristics of the cement. The total amount of alkalis expressed as Na₂O-equivalent was calculated following Ref. [26] and the result was 0.43%.

Table 1. Physical, chemical and mineralogical characteristics of Portland cement.

Constituent	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	SO ₃	MgO	K ₂ O
(wt%)	20.29	6.40	3.51	65.13	2.65	1.03	0.48
Constituent	Na ₂ O	P ₂ O ₅	TiO ₂	SrO	ZnO	Mn ₂ O ₃	LOI
(wt%)	0.12	0.03	0.26	0.03	0.01	0.06	3.13
Bogue Compounds	C ₃ S=55	C ₂ S= 16	C ₃ A=11	C ₄ AF=11	Physical Characteristics	Blaine 394 (m ² /kg)	Specific Gravity: 2.90
(wt%)							

2.1.2 Fine and Coarse Aggregates

The fine aggregate had an SSD specific gravity (SG) of 2.6 and an absorption capacity of 4.1%. Following recommendations for the design of high-strength concrete [27][28], the fineness modulus of the fine aggregate was as coarse as 3.0. The coarse aggregate was crush gravel with a maximum size of

9.5 mm, SG-SSD = 2.7, and absorption capacity of 4.2%. Both materials are in accordance with ASTM C33 [29]. As stated by Almusallam et al. [30] past studies demonstrated that mechanical properties of high-performance concretes are dependent on the quality of the coarse aggregate. Therefore, in the present research, the source of aggregates was the

same for the relatively large number of cylinders employed in the experimental program.

2.1.3 Mineral Admixtures

The nS consisted of nanoparticles in the form of opalescent and odorless amorphous silica dispersed in water (slurry). The micro-SiO₂ was conformed to ASTM C1240 [31] and was used in the form of uncondensed dry particles. The class F fly ash that was used was classified as low-calcium ASTM Standard C618 [32] (SiO₂ + Al₂O₃ + Fe₂O₃ ≈ 88%). Table 2 shows the principal physical and chemical characteristics of nS, SF, and FA. Fig. 1 shows results of x-ray diffraction (XRD) analysis of FA, SF, and nS powders. The main intensity peaks were associated to 2θ angles of 27°, 22° and 24° for FA, SF and nS, respectively.

Table 2. Principal physical and chemical characteristics of FA, SF and nS.

	FA	SF	nS
Chemical composition (wt%)			
SiO ₂	54.3	91.3	99.9
H ₂ O	0.7	0.3	---
pH	---	---	9.0
LOI	1.28	---	0.1
Physical properties			
Specific gravity	2.1	2.3	2.1
Mean size (nm)	25000	200	25
Retained #325 (%)	15.5	---	---
SSA (m ² /kg)	320	25000	109000

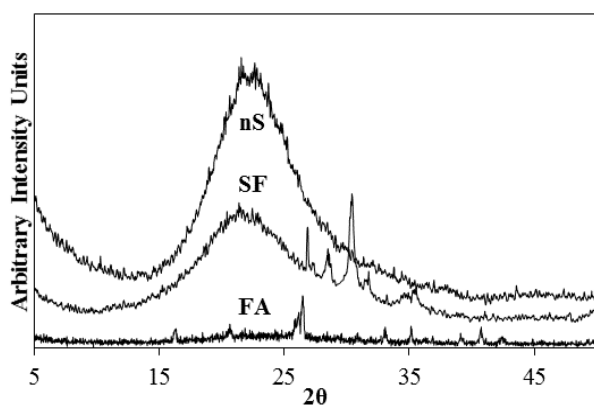


Figure 1. XRD pattern of fly ash and micro/nano-SiO₂ obtained with CuKα radiation.

2.1.4 Chemical Admixture

The SP was a carboxylate-polyether type copolymer conform to ASTM C494 [33] Types A and F and ASTM C1017 [34] type I with SG = 1.08, pH = 4.8-6.8, and 40% of dry active matter. It is commercially designed as a high-range water-reducing admixture (HRWRA).

2.2 Methods

2.2.1 Mix Proportions and Testing Procedures

All the data presented were obtained experimentally by the authors. All the concrete cylinders were cast and cured following the ASTM standard [35], and fractured in the same way in order to attain comparable results. The coarse-to-fine aggregate ratio was 1.50. The cementitious materials' amount was 465±5 kg/m³ at w/b = 0.35. The concrete constituents were mixed at two speeds i.e., 60 and 120 rpm in a commercial laboratory mixer. The total mixing time was fixed at 5 min. The concrete samples were prepared using the same steps in which 50% of the water and 100% of the fine and coarse materials were mixed for 1.5 min at 120 rpm. Cement was mixed in dry condition with SF (if used) and/or FA (if used), and then this powder mix was added to the mixer for 2 min at 60 rpm. The process was followed by addition of previously mixed remainder water with slurry nS (if used) and the corresponding SP dosage. Thereafter, the materials were mixed for 1.5 min at 120 rpm. The samples were cured in limewater at 23-25 °C. The proper amount of SP had been previously obtained in laboratory experiments for each mix design, higher workability without segregation or excessive bleeding was taken into account. The water content of the SP was accounted in all the mix designs. The fresh concrete was poured into ASTM standard cylinders having 50 mm of diameter and 100 mm in height for testing procedures conforming to ASTM [36]. After pouring and finishing, previously consolidation was carried out by the rodding method. The formwork removal occurred 24 h after casting. The samples were cured in limewater at 23-25 °C until the prescribed period of failure. The mechanical tests were carried out conforming the ASTM procedures for compression tests of the concrete cylinders [37]. Five different ages of testing were conducted in this research: 3, 7, 28, 56, and 90 days of curing using a 3000 kN Forney universal test machine operating in load-controlled setting. Mix proportions and compressive strengths

(Sc) are shown in Table 3.

Table 3. Mix proportions, DOE compositions, and compressive strengths at different ages.

Composition {nS:SF:FA}*	DOE	$\bar{Sc}$ (MPa)**				
		3 days	7 days	28 days	56 days	90 days
{0.0:0.0:0.0}	I-II-III	24.37	31.90	50.30	52.84	54.91
{3.0:0.0:0.0}	I-II-III	36.68	54.06	67.84	70.95	74.81
{6.0:0.0:0.0}	I-II	30.84	51.98	65.13	70.39	73.48
{0.0:0.0:20}	I-III	22.90	29.39	43.70	51.51	54.92
{0.0:0.0:40}	I	13.75	20.29	35.62	43.25	51.65
{3.0:0.0:40}	I	18.74	28.99	40.78	44.90	50.46
{3.0:0.0:20}	I-III	27.58	38.68	52.70	53.91	61.25
{6.0:0.0:40}	I	26.31	36.00	46.19	51.67	58.53
{6.0:0.0:20}	I	35.01	45.04	54.83	60.13	62.36
{0.0:10:0.0}	II-III	26.29	40.84	56.16	59.78	65.42
{0.0:20:0.0}	II	29.02	45.31	63.28	75.09	75.29
{3.0:20:0.0}	II	31.37	46.98	63.36	68.71	76.85
{3.0:10:0.0}	II-III	34.94	47.97	62.72	66.96	70.01
{6.0:20:0.0}	II	36.65	50.89	64.67	71.65	70.63
{6.0:10:0.0}	II	37.64	51.50	60.30	68.29	69.78
{1.5:0.0:10}	III	26.96	37.27	47.97	53.67	55.97
{0.0:10:20}	III	21.08	34.34	48.40	58.74	61.85
{0.0:5.0:10}	III	28.43	37.61	56.99	63.52	65.71
{1.5:5.0:0.0}	III	31.71	44.80	58.14	63.83	63.08
{1.5:10:10}	III	27.10	39.79	56.50	65.44	68.00
{1.5:5.0:10}	III	26.86	39.35	54.57	61.99	64.80
{1.5:5.0:20}	III	22.36	36.56	51.48	57.16	61.97
{3.0:5.0:10}	III	32.67	47.44	59.41	64.09	68.41
{3.0:10:20}	III	24.96	39.92	53.39	59.74	65.46

* Mix proportions are expressed as percentage of cementitious materials. ** The symbol $\bar{Sc}$ stands for average of three replicates.

2.2.2 Development of the ANN and DOE models

In this study, several back-propagation (BP) algorithms were tested in developing the ANN simulations. The BP learning law consists of adjusting the weights and bias values from the output layer toward the input vector by means of an iterative process [38][39]. The target is to minimize the mean squared error (MSE) in each iteration cycle until no further improvement is reached. The general performance of an ANN using BP can be explained as an input vector and a vector bias, at least one hidden layer of neurons, and at least one output (Fig. 2). Mathematically, the functioning of

the n -th neuron in the y -th layer is represented by Eq. (1), where m is the number of inputs that arrive at a neuron. A layer of a network includes the combination of the weights (w_{in}), the bias (b_n), the multiplication and summing operations between them, and the transfer function (f). The term $p_i^{(y-1)}$ refers to the signal from the i -th neuron in the previous layer ($y-1$) that could be the input vector or any hidden layer. The bias term accounts for the parameters whose contribution to the output is either unintentionally missed or cannot be calculated. The vector bias is summed with the weighted inputs to form the net input vector, which is the argument of

the transfer function [40]. This latter function takes the argument and produces the output vector (o) (Eq. 1). In the vector input, each neuron receives the variable to be analyzed, whereas the outputs from these first neurons serve as the inputs in the subsequent hidden layers. Finally, the output of the neuron in the last layer is the target that is being sought (Fig. 2).

$$o_n^{(y)} = f(b_n^{(y)} + \sum_{i=1}^m w_{in}^{(y)} p_i^{(y-1)}) \quad (1)$$

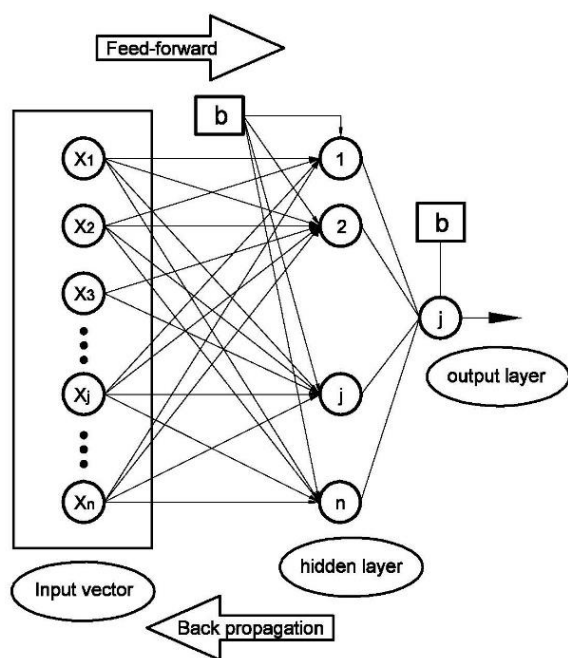


Figure 2. Schematic of a multilayer feed-forward/back-propagation neural network model.

The architecture of a network is the number of layers, the number of neurons, and the type of the transfer function in each layer of a particular network. No unique universal architecture exists; this is a function of each particular problem [15]. Hence, finding the optimum number of neurons in the hidden layer, the number of hidden layers, and the type of transfer function are part of the most complex tasks in ANN simulations [14]. Training the network consists of using a known set of input and output datasets, by means of an iterative process, the optimal set of weight and bias values are reached following a computational algorithm. It is important to note that this algorithm also should be adequately selected to obtain a satisfactory performance of the network. The training process of an ANN can be regarded as solving a complex

nonlinear least-square mathematical problem with the difference between the actual and simulated outputs acting as the performance for the problem [41]. In creating an effective network, the training step must be carefully developed because the error surface can converge to a false minimum or to a true minimum but very slowly [10]. Also, the accuracy of the network predictions is strongly related to the selection of the weights in the algorithm [40]. Nevertheless, once the optimum architecture is found, the ANN model is an extremely efficient nonlinear statistical tool for use in complex problems [10][14][15][19][40].

One problem that can occur when training neural networks is that the network over-fits on the training set and does not generalize well to new data [19]. This can be prevented by using computational techniques that usually require a large set of data, which is divided between training and testing sets [42][43][44]. Although the number of data was adequate to perform the DOE methodologies with three replicates and center points, the present study has a relatively limited number of experimental data for the ANN approach. Nevertheless, this was successfully overcome by employing an exhaustive computational preliminary work by testing the convergence of the ANN simulations on several different algorithms, starting from 1 to 20 hidden neurons and from 1 to 2 hidden layers. Also, in view of a certain degree of randomness involved in the development of any ANN model, each one of the trial architectures was studied from at least twenty initial random points in order to avoid false minimum or other local attractors. The separation between training, validation, and testing datasets was: 75%, 5%, and 20% of the total samples data, respectively. The relatively small sample size put an additional challenge to the ANNs that have to be better than 15 DOEs working simultaneously and at the same time the ANN had to show a good generalization capacity. As stated earlier, three independent design of experiments were conducted in the present study for each age of testing (3, 7, 28, 56, and 90 days), referenced hereafter as the following: DOE I consisting of nS(0.0-6.0 wt%)-FA(0.0-40.0 wt%), DOE II consisting of nS(0.0-6.0 wt%)-SF(0.0-20.0 wt%), and DOE III consisting of nS(0.0-3.0 wt%)-SF(0.0-10.0 wt%)-FA(0.0-20.0 wt%). The central composite design models (DOEs I and II) consisted of three replicates with 12 cube points, 3 center points, and 12 axial points with 2

factors (nS/SF, nS/FA). DOE III consisted of three replicates with 24 cube points, 3 center points, and 18 axial points with 3 factors (nS/SF/FA). A total of 27 and 45 runs were conducted randomly within a unit statistical block for DOEs I-II and DOE III, respectively. For all the DOEs, the α -value was set equal to 1 (face-centered). The DOE models were developed in MINITAB® v. 16 statistical software and STATGRAPHICS® CENTURION XV of StatPoint Co. statistical software.

The ranges of the interval values used in each experimental design were selected according to field and literature considerations. The replacement levels commonly employed in the concrete technology industry and related literature are for SF ranges from 5-30 wt% [7][27][45][46]. Replacement levels for FA ranging between 10-40 wt% [5][28][47] are found in field and literature reports, 15 wt% being the usual dosage employed in high-performance concrete [27]. DOE compositions are shown in Table 3. It is important to note that, in the philosophy of the design called High-Volume Fly Ash Concrete (HVFA), the replacements levels of FA (usually Class F) in the mixes normally start at 50 wt% [48][49]. Nevertheless, the designs presented here do not follow the HVFA approach. Additionally, although nS are somewhat new materials in concrete investigations, their most common replacement levels reported in literature and field applications range from 0.5 to 5 wt% [9][24]. For the response variable, the significant terms in the models were found using analysis of variance (ANOVA) and second-order regression analysis. The statistical criterion for factor effect rejection was when their p-values (observed significant level) were greater than 0.05.

In the developing of the ANN-models, all the data points (average of three replicates) of the above DOEs were considered for training, validation, and testing. Many authors [15][38][50][51][52][53] widely recommend that data be normalized before training to prevent extreme numerical values or ranges of any particular parameter from distorting the influence of the other parameters. Hence, the input and output values were normalized (Eq. 2) [52] in the range of [-1, +1] before any numerical simulation were conducted. In the normalization function (Eq. 2), v_i^{norm} and v_i are the normalized and un-normalized values, respectively, of the input/output variables, and v^{min} and v^{max} are the

minimum and maximum variable values, respectively.

$$v_i^{norm} = \frac{2(v_i - v^{min}) - (v^{max} - v^{min})}{(v^{max} - v^{min})} \quad (2)$$

In this study, multilayer feed-forward back-propagation neural network is used with a nonlinear logistic sigmoid function (Eq. 3) as the transfer function for the input vector-hidden layer and the identity function as the transfer function for the hidden layer-output layer. The sigmoid activation function is a continuous function often utilized in nonlinear problems because its derivatives can be determined without major computational demand [54]. The ANN was implemented using scripts in MATLAB® v.7.1. During training, the stopping criterion was set to finish when one of the following criteria was met, i.e., the MSE $\leq 1 \times 10^{-4}$, the gradient value was less than 1×10^{-9} , or the iteration numbers were larger than 1000. In addition to reinforce the accuracy of the architectures, the ANN-simulated outputs were compared with each one of the outputs from the DOEs by mean of the Pearson's correlation coefficient (Eq. 4). In this study, three statistical criteria were selected to compare the ANN simulations results (Sp) with the laboratory results (Sm) at training, validation, and testing steps, i.e., the root-mean-square error (RMSE) in MPa (Eq. 5), the coefficient of efficiency (CE) (Eq. 6), and the Pearson's correlation coefficient (r) (Eq. 4).

$$f_n^{(y)} = \frac{1}{1 + \exp[-(b_m^{(y)} + \sum_{i=1}^m w_{in}^{(y)} o_i^{(y-1)})]} \quad (3)$$

$$r = \frac{\sum_{i=1}^N (Sm - \overline{Sm})(Sp - \overline{Sp})}{\sqrt{\sum_{i=1}^N (Sm - \overline{Sm})^2 \sum_{i=1}^N (Sp - \overline{Sp})^2}} \quad (4)$$

$$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N (Sp - Sm)^2} \quad (5)$$

$$CE = \frac{\sum_{i=1}^N (Sm - \overline{Sm})^2 - \sum_{i=1}^N (Sm - Sp)^2}{\sum_{i=1}^N (Sm - \overline{Sm})^2} \quad (6)$$

$\overline{Sp}$ and $\overline{Sm}$ represent the average of the measured values for compressive strength (MPa) from ANN simulations and laboratory experiments, respectively. N is the total number of observations in training, validation, or testing datasets. RMSE has the advantage that larger errors receive much greater

attention than small ones [53]. Pearson's correlation coefficient is a measure of the linear correlation between the ANN simulations and the raw data. In general terms, the correlation values suggest a tendency of the data to plot on a 1:1 straight line when a value tending toward the unit indicates a good linear fit [51]. The coefficient of efficiency is a relative error measure, which in conjunction with RMSE, i.e., a measure of the absolute error, makes the assessment of the models more rigorous [55].

In addition to testing dataset in the ANN models and testing in the DOE statistical softwares, a sensitivity analysis based on the connection weight approach [56] was performed to identify the most important input parameters from the ANN approach. Several different weight and bias values were generated randomly as starting points in order to select the best performance of the trained network parameters. Each one of these random points was checked to meet the aforementioned tolerance stopping criteria. Once the architecture was defined, the actual values of input vector-hidden layer and hidden layer-output layer weights of trained ANN models were used to select the most important input variables following the connection weights and biases procedure, as explained later. A key reason behind the development of the ANN models is related to their potential applicability in conjunction with DOEs. The major importance lies at the moment of making a decision about the pertinence of the most common variables employed in concrete technology in the DOE analysis and their possible relationship with the LOF generally exhibited by some complex cementitious systems.

3. RESULTS AND DATA ANALYSIS

3.1 DOE Analysis

Table 4 shows the compression results from the DOE analysis. In this table, the sign associated with the p-values indicates the positive/negative contribution of each particular term to the strength development. The orthogonality condition was successfully found in all DOEs. The independence, equal-variance, and normality assumptions were carefully checked for each DOE. The linear, interactive, and quadratic regression effects are shown with their associated p-values and Pearson's correlation coefficients. The constant term is not shown due to space considerations but was significant (p-value < 0.05) at all ages and for all

designs. The results show the input variables exhibited through the time a variety of p-values, Pearson's values, and linear, interactive, and/or quadratic effects. The continuous changing of the surface responses as the concrete aged (Figs. 3-7) makes the ANN models plausible candidates to be employed as an auxiliary nonlinear statistical tool. Also, the motivation was that all the models showed a LOF of second-order (Table 4). The reader is advised that in Table 4, the DOEs I and II present some empty spaces because SF and FA were not designed input variables for I and II models, respectively. In the development of the second-order polynomial models, the ANOVA results in Table 4 showed that the most important parameters influencing the compressive strength (p-value < 0.05) at all ages were the linear terms of nS and FA and the interactive term nS·SF. Also, the quadratic term of the nS variable (nS·nS) was important for most ages, with minor participation of the quadratic term (SF·SF). The quadratic term of FA (FA·FA) and the interaction between the SF and FA (SF·FA) played a less important role on the strength development in the present study (p-value ≥ 0.05).

It is important to note that the environmental capabilities and the fresh state benefits of the FA motivate the employment of this material in conjunction with nS particles. That is, the FA offers a potential for high replacement levels of cement in a mix design up to 70 wt% [57][58]. Nevertheless, the expected consequence will be a drop in the compressive strength due to the reduced activity of the FA compared to Portland cement, at least at early ages of curing [57][58]. Then, based on the extremely high reactivity capacity of the amorphous nanosilica particles [59][60], the use of nS could be expected to compensate for this negative effect induced by the high FA replacement to Portland cement. Nevertheless, in the present work the statistical results showed that nS particles produced a negative effect on strength development when combined with the FA, as revealed by the nS·FA interactions (p-value < 0.05). Thus, when the FA replacement is at the highest level, i.e., 40 wt% (DOE I), the presence of nS either at the highest (nS = 6.0 wt%) or the lowest level (nS = 0.0 wt%) is not statistically significant at early ages (p-value ≥ 0.05). Only at 90 days does this effect become statistically significant but with negative contribution to strength development. Conversely, at lower FA and nS replacement levels (DOE III), the

interaction effect of these two variables is effectively significant (p -value < 0.05) at all ages. Nevertheless, as in the DOE I, the interaction effect

is negative on the strength gain (Figs. 8b-12b).

Table 4. Results of p -values and Pearson's correlation coefficients from DOEs in compression tests.

Age	DOE	nS	SF	FA	nS·SF	nS·FA	SF·FA	nS·nS	SF·SF	FA·FA	LOF	r
3d	I	0.00(+)	---	0.00(-)	---	0.08(+)	---	0.08(-)	---	0.01(-)	0.00	0.93
	II	0.00(+)	0.20(+)	---	0.88(+)	---	---	0.01(-)	0.29(-)	---	0.00	0.88
	III	0.00(+)	0.14(-)	0.00(-)	0.08(-)	0.00(-)	0.07(-)	0.00(+)	0.01(-)	0.01(-)	0.00	0.96
7d	I	0.00(+)	---	0.00(-)	---	0.23(-)	---	0.00(-)	---	0.70(-)	0.00	0.97
	II	0.00(+)	0.28(+)	---	0.00(-)	---	---	0.01(-)	0.95(+)	---	0.00	0.90
	III	0.00(+)	0.00(+)	0.00(-)	0.00(-)	0.00(-)	0.28(+)	0.02(+)	0.00(-)	0.78(-)	0.00	0.97
28d	I	0.00(+)	---	0.00(-)	---	0.19(-)	---	0.00(-)	---	0.61(+)	0.00	0.97
	II	0.00(+)	0.08(+)	---	0.00(-)	---	---	0.00(-)	0.04(+)	---	0.00	0.86
	III	0.00(+)	0.00(+)	0.00(-)	0.00(-)	0.02(-)	0.29(+)	0.00(+)	0.00(-)	0.59(-)	0.00	0.93
56d	I	0.00(+)	---	0.00(-)	---	0.10(-)	---	0.40(-)	---	0.80(+)	0.01	0.91
	II	0.00(+)	0.01(+)	---	0.00(-)	---	---	0.21(-)	0.11(+)	---	0.02	0.81
	III	0.00(+)	0.00(+)	0.00(-)	0.04(-)	0.00(-)	0.09(+)	0.23(+)	0.04(-)	0.18(-)	0.01	0.86
90d	I	0.00(+)	---	0.00(-)	---	0.02(-)	---	0.08(-)	---	0.48(+)	0.00	0.92
	II	0.00(+)	0.00(+)	---	0.00(-)	---	---	0.00(-)	0.03(+)	---	0.00	0.93
	III	0.00(+)	0.00(+)	0.00(-)	0.00(-)	0.01(-)	0.27(+)	0.01(+)	0.06(-)	0.15(-)	0.00	0.89

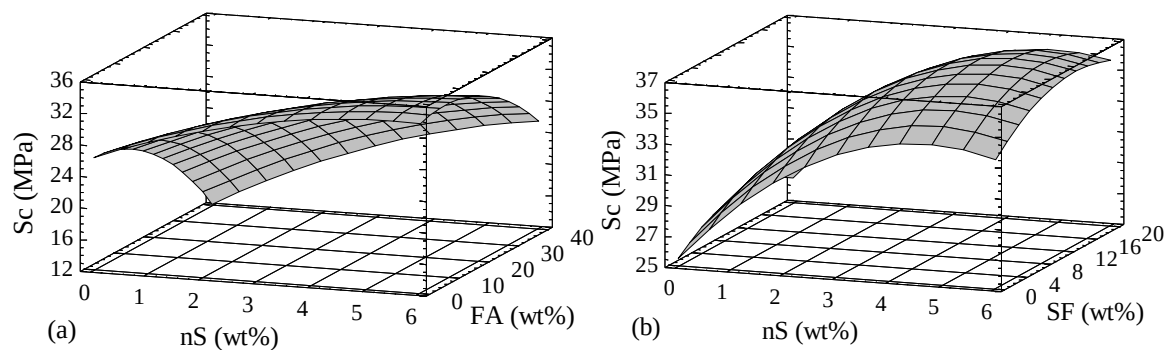


Figure 3. Compressive strength of concretes at 3 days: (a) for DOE I and (b) for DOE II.

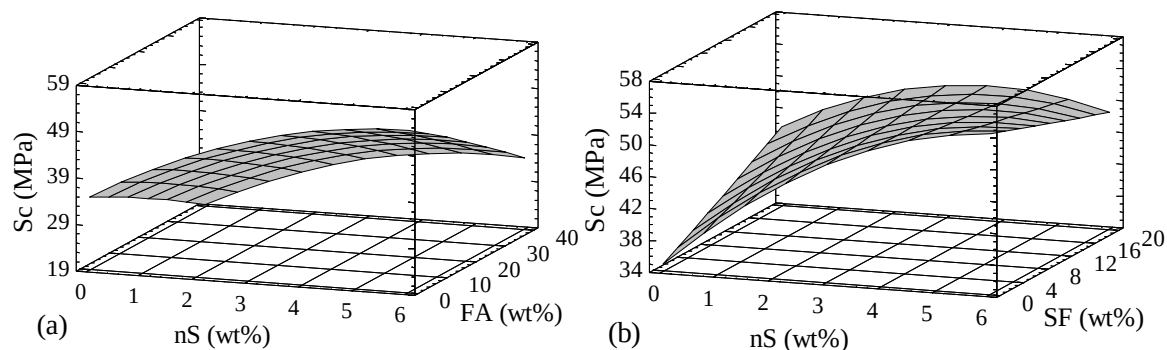


Figure 4. Compressive strength of concretes at 7 days: (a) for DOE I and (b) for DOE II.

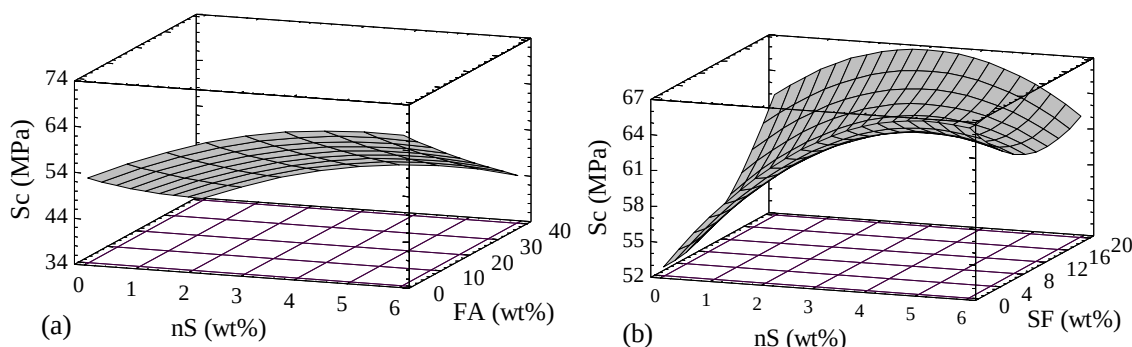


Figure 5. Compressive strength of concretes at 28 days: (a) for DOE I and (b) for DOE II.

Taken into account the FA presence, which usually develops its pozzolanic potential at ages beyond 28 days [27][28][61], in this particular study regardless of the testing time (3 or 90 days) and the nS presence, the FA performance is unclear as can be seen from the experimental results. Also, the quality of the particular FA employed is questionable, as hinted by the morphology in the XRD pattern (Fig. 1) and the amount of noncrystalline silica (Table 2). These observations on the quality of the FA are in agreement with Aitcin [27] who reported that the FA is one of the most variable and least reactive cementitious materials when compared to slag or SF. At least under the present experimental w/b conditions, age of testing (up to 90 days), and proportions of the combined use of nS and FA, the present results were not favorable. It could be surprising, but a previous research carried out by Kawashima et al. [62] showed that the conjunction use of FA and nS resulted in less pozzolanic activity of the FA after 7 month of maturity. The study demonstrated that due to the presence of 5% nS a double-layer shell structure coated the FA particles, therefore the pozzolanic activity suffered detriment when compared with samples having FA additions but without nS. A similar phenomenon could be present in our research. This is of extreme importance for concrete technology because the nS properties, such as its high surface energy and therefore, its high reactivity capacity could be of interest in mixes with low cement and/or HVFA which are highly FA systems. Nevertheless, more extensive research on the interaction between FA and nS from different sources and at different proportions should be conducted to check this potential harmful phenomenon.

Figs. 3-7 show the strength development through

time for DOEs I and II. The surfaces are shown regardless of the p-value. Nevertheless, the analysis in the present study was conducted at the 95% level of confidence. In general terms, it can be noted that, based in the p-value, the most influential linear terms in all models at all ages were the nS and FA contents. The contribution of nS to compressive strength gain is notable while the FA input variable was related to negative influence at all ages. The negative effect of FA is expected at early ages due to the high replacement levels of cementitious material (up to 40 wt%) and the recognized low reactivity of the FA at those early ages [27][57][58]. Nevertheless, the behavior of FA systems was not satisfactory even at ages as long as 90 days (Figs. 3a-7a). The SF had a positive effect being the third statistical ranking linear term in participation on strength development. The statistical significance of the SF variable was noted at 56 days old (Fig. 6b) for high amounts of both nS and SF (DOE II). This could be explained because the extremely high surface energy of the nS particles jeopardized the lower (relative) surface energy of the SF particles, thus its contribution was delayed in the statistical analyses. For small amounts of both nS and SF (DOE III), the SF started to be important at 7 days (Fig. 9b). This latter age is related to the normal rate for the pozzolanic development in SF systems [30].

Laboratory compressive strength values and data from DOEs I and II (Table 4) at all ages exhibited a strong correlation, as reflected by the large r-values [63] (i.e., $r > 0.80$). From a statistical point of view, this represents a good agreement between the model outputs and the experimental results. Nevertheless, the LOF tests revealed that points different from those defined in the inputs cannot be properly represented by the surface generated by the second-

order model. Also, DOE III, which has reduced the highest values of the input variables, induced a change only in the interactive and quadratic effects (Figs. 8-12), altering some answers regarding the DOEs I and II. However, the LOF condition remained unchanged. In addition, by changing the upper limits of the variables in the DOE III, the

scatter in the compressive strengths of the systems was larger than in DOEs I and II. This observation takes into account that the Pearson's correlation coefficients were lower in DOE III than in DOEs I and II for all ages, except 3 days.

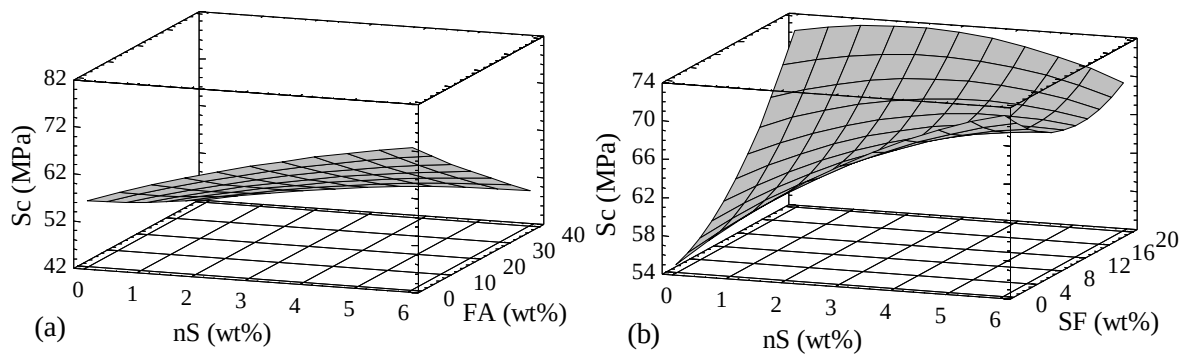


Figure 6. Compressive strength of concretes at 56 days: (a) for DOE I and (b) for DOE II.

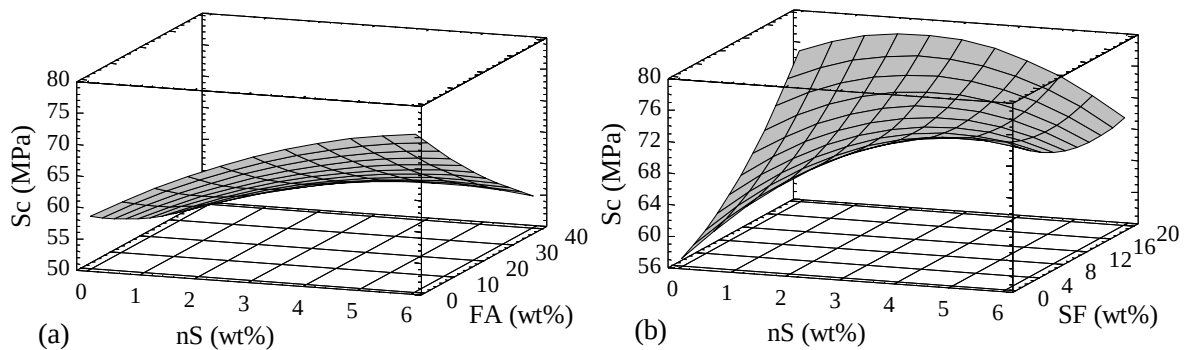


Figure 7. Compressive strength of concretes at 90 days: (a) for DOE I and (b) for DOE II.

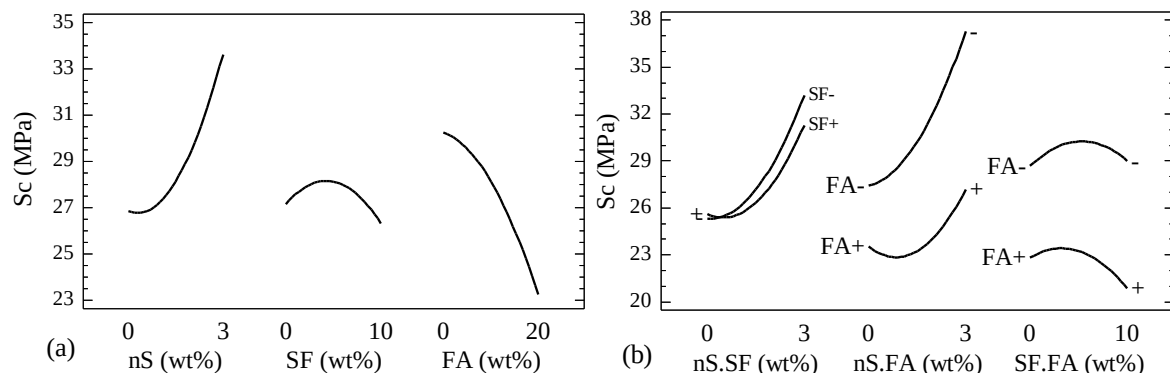


Figure 8. Compression analysis from DOE III at 3 days: (a) principal effects and (b) interactive effects.

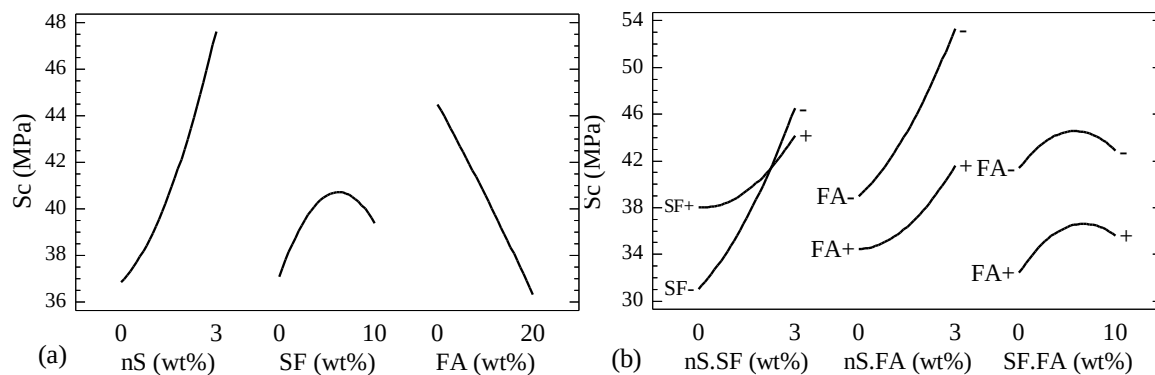


Figure 9. Compression analysis from DOE III at 7 days: (a) principal effects and (b) interactive effects.

The simultaneous incorporation of nS, SF, and FA in the DOE III analysis can be seen in Figs. 8-12. In part (b), the sign of the variable indicates the low (-) or high (+) level of replacement for each one. The surface response for the DOE III in the replacement levels employed here showed statistically significant curvature effects (Table 4 shows the corresponding p-values). These effects are more pronounced as the concrete gained pozzolanic activity, i.e., from 7 days of testing (Figs. 9b-12b). The weighted statistical participation of the nS as principal effect is again noticeable. As for DOEs I and II, the nS presence had a positive effect on strength development. The FA as a linear variable was also significant, but contrarily to nS, FA particles induced a negative effect on strength gain at all ages. Finally, in this segment research, the SF was the least statistically active variable, although its contribution was positive on the strength development. Another important feature regarding the SF additions is that, at higher levels of replacements (DOE II), this variable is active only after 56 days of age. On the other hand, at lower levels of replacements (DOE III), the SF variable is statistically active from the early age of 7 days (Figs. 9a-12a). This can be attributed to more effective particle dispersion at lower dosages.

3.2 ANN Simulations

ANNs are often called “black box” [64][65], but a sensitivity analysis of the bias and weights [20][56][65] in conjunction with another robust statistical tool, such as experiments design, allows the behavior of the parameters to be clarified considerably whereas the prediction models allow a better understanding of the overall complex system behaviors. Since the experimental ranges and/or the input variables were changed in all the DOE

analyses and these ranges were taken into account from field values and not only based on laboratory considerations, it can be concluded that changing the experimental intervals is not a plausible option in order to overcome the technical difficulties associated with the LOF in the DOEs. In this sense, the LOF condition is more appropriately interpreted as variance inside the systems additional to the contributions generated by the terms that were considered. Then, the ANN models are expected to help in the understanding of the physical phenomenon by including other input variables in addition to those taken into account in the DOE analysis.

In concrete technology, it is well known that mechanical and durability properties of the concrete depend on the materials' quality, mix proportions, and the fresh state properties. Regarding fresh state properties, this work proposes considering eight new input variables in order to get more information about the mechanical compression in the hardened state. Also, the maturity age of the concrete had to be considered as an input variable for technical reasons associated with the ANN models. In Table 5, the input variables are nS (nano-SiO₂), SF (micro-SiO₂), FA (Class F fly ash), PC (Portland cement type I), WT (added water), AG (the sum of fine and coarse aggregate contents), SP (superplasticizer), UW (unit weight conforming to ASTM C138 [67], AC (entrapped air content conforming to Ref. [67], FT (flow table test as described in ASTM C1437 [68], IS (initial slump from the slump-cone test conforming to ASTM C143 [69]), and MA (maturity of the concrete at the time of the compression test). The full set of old and new input variables along with their ranges and units are shown in Table 5.

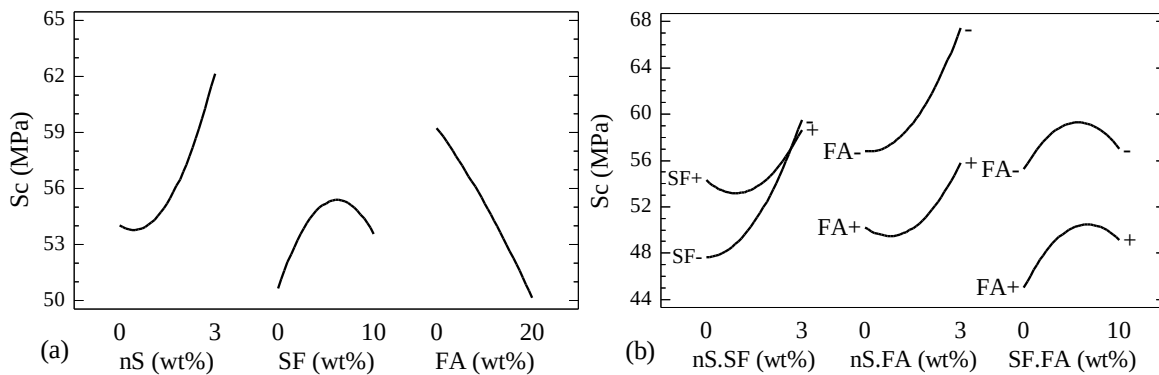


Figure 10. Compression analysis from DOE III at 28 days: (a) principal effects and (b) interactive effects.

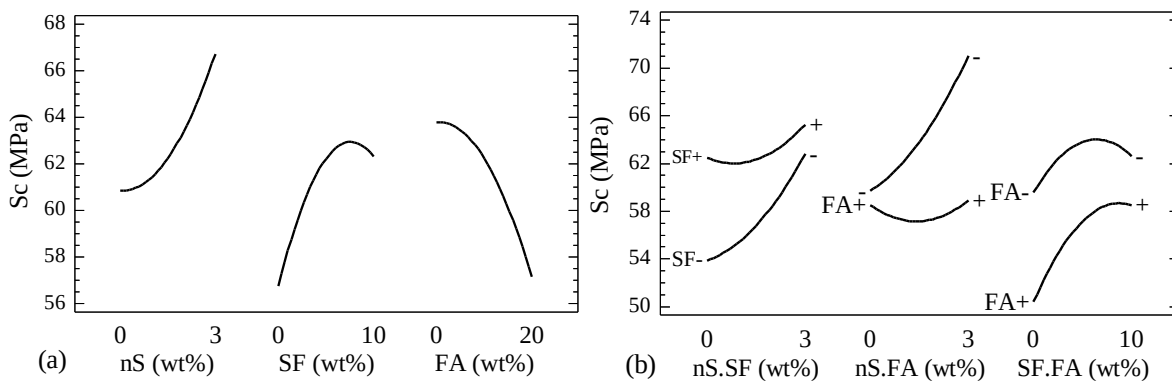


Figure 11. Compression analysis from DOE III at 56 days: (a) principal effects and (b) interactive effects.

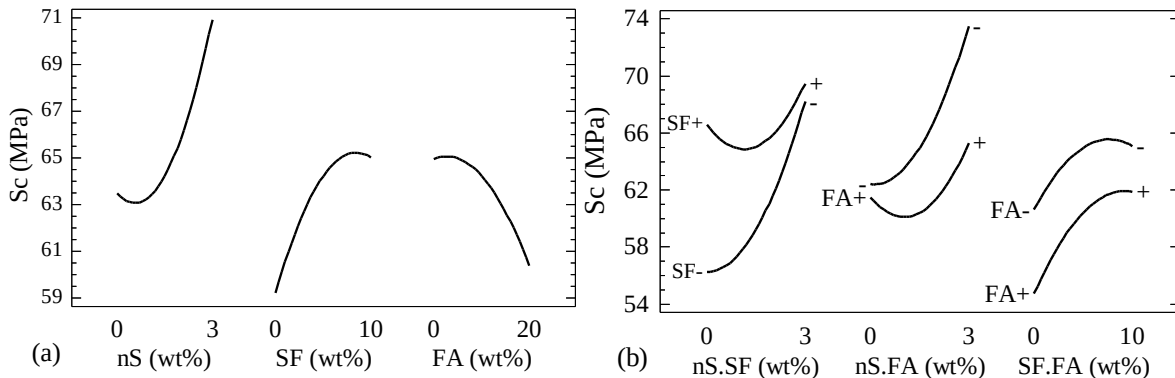


Figure 12. Compression analysis from DOE III at 90 days: (a) principal effects and (b) interactive effects.

All the increment steps of the new input parameters are variable in nature, i.e., none was systematic. In the WT variable, the water contents of the nS (slurry) and the SP were taken into account as well as the absorption requirements by the aggregates. Although the flow table test is employed in cement mortars, in the present study on concrete samples this technique was adopted due to its valuable information on the fresh state in cementitious

mixtures. Also, the adoption of the test was reasonable because the maximum aggregate size was 9.5 mm; this means that it is a relatively small particle to be employed in the flow table test. The output of the ANN models is compressive strength (S_c) in MPa, as a function of the mix design components, fresh state properties, and the age at mechanical testing. All the samples were produced, cured, and tested following standard ASTM

protocols in order to obtain an unbiased comparison between and within them. In addition to helping to overcome the LOF condition, ANN simulations are advantageous in providing a single equation to represent all the input variables for the development of the model. In the developing of the ANN models, several simulations were conducted to obtain the response variables using different algorithms and different architectures (arrays) within each algorithm. Also, each algorithm had at least twenty randomly selected initial points for its initialization. In order to find the net's architectures, the widely used trial-and-error method was employed. Based on the parameters shown in Table 5, back-propagation algorithms (BPA) such as gradient descent with momentum BPA, resilient BPA, Fletcher-Reeves and Polak-Ribière conjugate gradient BPAs, quasi-Newton BPA, and one-step secant BPA were tested (not shown here). Each of the above BPAs were tested using 1 to 20 hidden neurons, in one and two hidden layers and several values for internal parameters such as learning rate and momentum (values taken from literature). Nevertheless, the performance was not satisfactory because the convergence rate was very slow or the output showed low precision.

Table 5. Design parameters of ANN models.

Variables	Minimum	Maximum	Unit
Inputs			
nS	0.0	28.2	kg/m ³
SF	0.0	93.8	kg/m ³
FA	0.0	187.6	kg/m ³
PC	253.0	469.1	kg/m ³
WT	173.0	220.1	kg/m ³
AG	1585.9	1672.7	kg/m ³
SP	2.8	18.4	kg/m ³
UW	2284.0	2391.0	kg/m ³
AC	3.9	7.1	%
FT	84.0	138.0	%
IS	101.6	130.2	mm
MA	3.0	90.0	days
Output			
Sc	13.8	76.8	MPa

In this study the best performance was obtained by using the Levenberg-Marquardt (LM) BPA.

Nevertheless, Bayesian regularization (BR) algorithm (BRA) in combination with early stopping proved to be the most stable and satisfactory algorithm tested. Although no longer required in the BRA, the early stopping was maintained to provide a reasonable basis for comparison among all the algorithms tested. In this sense, the entire algorithms tested had the same number of training (75%), validation (5%) and testing points (20%). These two algorithms, i.e., LMBP and BRA, will be discussed later. In general terms, data for compressive strength using both LMBP and BRA were successfully modeled as compared with the actual data from laboratory experiments. The average results for twelve randomly initial points and internal arrays between training, validation and testing datasets are shown in Table 6. Also, the results from ANN simulations resulted in better performance than results from the fifteen simultaneously DOEs, when compared with the Pearson's correlation coefficients in both aspects as adjusted and predictive models (Tables 7 and 8).

From Table 6, values for RMSE, CE, and *r* are shown for the best architectures. From this table it is possible to conclude that, in the present work, ANN simulations were suitable computer tools and could adequately predict compressive strength behavior of ternary and quaternary concrete mix designs with values being very close to the actual data. This is in accordance to similar works conducted using ANN or in general intelligent-based modelling methods to predict concrete compressive strength [17][19][20][54][70][71][72][73][74]. For the sake of comparison, Tables 7 and 8 show the Pearson's correlation coefficient values for compression analysis using both DOE methodology and the ANN simulations from the trained networks stated on Table 6. Table 7 shows the *r*-values for the adjusted models from each DOE, whereas Table 8 shows the *r*-values from the DOEs as predictive models. For the ANN simulations, each *r*-value for any particular age of testing was the average of twelve randomly simulations one of which being better than the fifteen *r*-values from the DOEs. In this work, the requirement imposed on the ANN models was extremely high because in a single equation, the performance of the net is compared against the accuracy of three simultaneous experimental designs conducted at each day of test. With five days of testing and each day having three DOEs, this means that each ANN model had to be better than fifteen

DOEs.

Table 6. Performance of ANN architectures (average of twelve simulations).

ANN Model	Training dataset			Validation dataset			Testing dataset		
	RMSE (MPa)	CE	r	RMSE (MPa)	CE	r	RMSE (MPa)	CE	r
LMBP [12:15:1]	1.578	0.989	0.995	1.499	0.989	0.996	2.384	0.972	0.987
BRA [12:3:1]	1.755	0.987	0.994	1.584	0.989	0.999	2.301	0.974	0.988

Table 7. Results between the adjusted model from DOEs analyses and ANN-models.

DOE	Age (days)	Adjusted r-DOE	Levenberg-Marquardt		Bayesian Regularization	
			r-ANN*	r-ANN/r-DOE	r-ANN*	r-ANN/r-DOE
I	3	0.9341	0.9886	1.0584	0.9842	1.0537
I	7	0.9668	0.9927	1.0268	0.9936	1.0277
I	28	0.9722	0.9789	1.0069	0.9831	1.0112
I	56	0.9100	0.9865	1.0841	0.9874	1.0851
I	90	0.9160	0.9878	1.0784	0.9894	1.0801
II	3	0.8174	0.9800	1.1989	0.9732	1.1906
II	7	0.8954	0.9797	1.0942	0.9837	1.0986
II	28	0.8603	0.9454	1.0989	0.9468	1.1005
II	56	0.8099	0.9673	1.1944	0.9782	1.2078
II	90	0.9271	0.9641	1.0399	0.9761	1.0528
III	3	0.9567	0.9661	1.0098	0.9582	1.0015
III	7	0.9661	0.9793	1.0136	0.9747	1.0089
III	28	0.9246	0.9533	1.0310	0.9513	1.0289
III	56	0.8570	0.9524	1.1113	0.9647	1.1257
III	90	0.8872	0.9489	1.0696	0.9500	1.0708
			average	1.0744	average	1.0763

* Average of twelve simulations.

Table 8. Results between the predictive model from DOEs analyses and ANN-models.

DOE	Age (days)	Predictive r-DOE	Levenberg-Marquardt		Bayesian Regularization	
			r-ANN*	r-ANN/r-DOE	r-ANN*	r-ANN/r-DOE
I	3	0.8901	0.9886	1.1107	0.9842	1.1057
I	7	0.9457	0.9927	1.0497	0.9936	1.0507
I	28	0.9529	0.9789	1.0273	0.9831	1.0317
I	56	0.8407	0.9865	1.1734	0.9874	1.1745
I	90	0.8588	0.9878	1.1502	0.9894	1.1521
II	3	0.6723	0.9800	1.4577	0.9732	1.4476
II	7	0.8243	0.9797	1.1885	0.9837	1.1934

Table 8. Cont.

DOE	Age (days)	Predictive r-DOE	Levenberg-Marquardt		Bayesian Regularization	
			r-ANN*	r-ANN/r-DOE	r-ANN*	r-ANN/r-DOE
II	28	0.7492	0.9454	1.2619	0.9468	1.2637
II	56	0.6384	0.9673	1.5152	0.9782	1.5323
II	90	0.8761	0.9641	1.1004	0.9761	1.1141
III	3	0.9266	0.9661	1.0426	0.9582	1.0341
III	7	0.9409	0.9793	1.0408	0.9747	1.0359
III	28	0.8748	0.9533	1.0897	0.9513	1.0874
III	56	0.7359	0.9524	1.2942	0.9647	1.3109
III	90	0.8046	0.9489	1.1793	0.9500	1.1807
			average	1.1788	average	1.1810

* Average of twelve simulations.

3.2.1 Levenberg-Marquardt Algorithm

Using the LM algorithm twelve input variables and one output neuron were used as fixed numbers and the best architecture consisted of one hidden layer with fifteen hidden neurons (HN); all these parameters are symbolized hereafter as LMBP[12:15:1]. This algorithm was stable only after 13 HN, and the architecture was defined as the smallest number of HN maintaining the RMSE, CE and r-values with high performance in the training, validation, and testing datasets. Also, this architecture was the most stable. Fig. 13 shows a graphical representation of one of the twelve architectures LMBP[12:15:1] of the trained (Fig. 13a) and tested (Fig. 13b) datasets. The values

obtained from the trained and tested datasets using ANN simulations are very close to the experimental values obtained in laboratory conditions. The graphical representation for the validation data was omitted due to its small size (5% of the total data), but its global behavior was comparable to the training data (Table 6). In the r-values from DOEs analysis versus LMBP-ANN simulations, the result was satisfactory with all the r-values from the net's architecture being higher than those obtained from DOE analysis (Tables 7 and 8). Also, Table 8 shows the better performance of the ANN simulations as predictive models when compared with the predictive capacity of the DOEs.

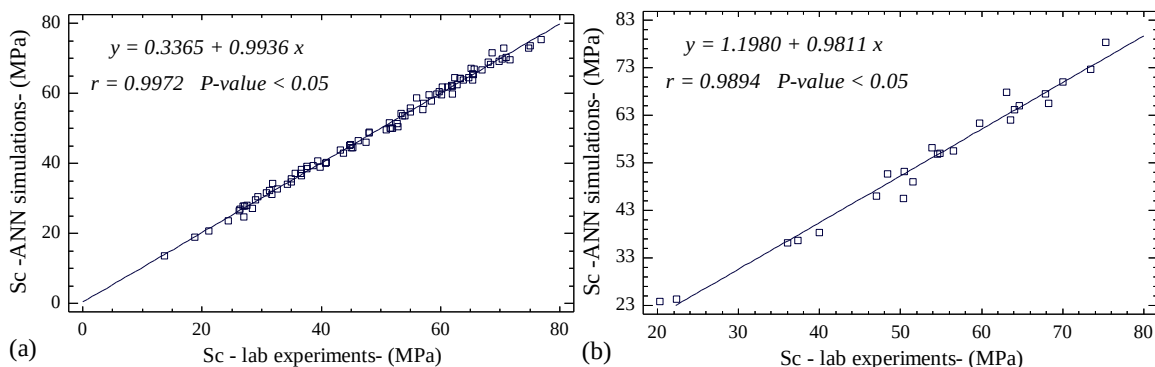


Figure 13. Scatter of actual values of concrete compressive strength and ANN simulated using LMBP[12:15:1] (a) trained dataset (b) tested dataset.

3.2.2 Bayesian Regularization Algorithm

Using the BR algorithm, twelve input variables and one output neuron were set as fixed numbers while the best architecture consisted of one hidden layer with three HN, that is, BRA[12:3:1]. This algorithm was stable from 2 to 9 HN, and the architecture was defined as the smallest number of HN without detriment in the RMSE, CE and r-values in global form (training, validation and testing). Nevertheless, using 4 or 5 HN the precision in training could be improved (not shown here) with insignificant detriment of the validation and testing sets, but the present architecture was defined ([12:3:1]) because of the excellent stability and simplicity. An ANN model of the BRA[12:3:1] architecture is represented in Fig. 14. In the figure are shown the results of the trained (Fig. 14a) and tested (Fig. 14b) datasets. As in the case for LMBP, the values obtained from the trained and tested datasets using BRA are very close to the actual values. As in LMBP, the graphical representation for the validation data is omitted due to its small size (5%

of the total data) being that their overall behavior was better than both the tested and trained datasets (Table 6). With regard to DOEs analysis versus ANN simulations, the results were satisfactory with all the r-values from the BRA being higher than the r-values from DOE analysis (Tables 7 and 8). In a similar fashion, the performance of the BRA was slightly better than the LMBP as compared with the average r-value ratios from Tables 7 and 8, i.e., $LMBP(r-ANN/r-DOE) < BRA(r-ANN/r-DOE)$. Even though the particular run illustrated in Figures 13 and 14 for LMBP and BRA, respectively; seems to show that the precision of the LMBP was higher than the BRA, in general terms (average), the result is the opposite. In this sense, the performance of the LMBP had two principal disadvantages with regard to BRA, i.e., (i) the performance as compared to DOE analysis was slightly inferior (Tables 7 and 8) and (ii) LMBP required a higher number of HN than BRA (Table 6) when the algorithm was stable.

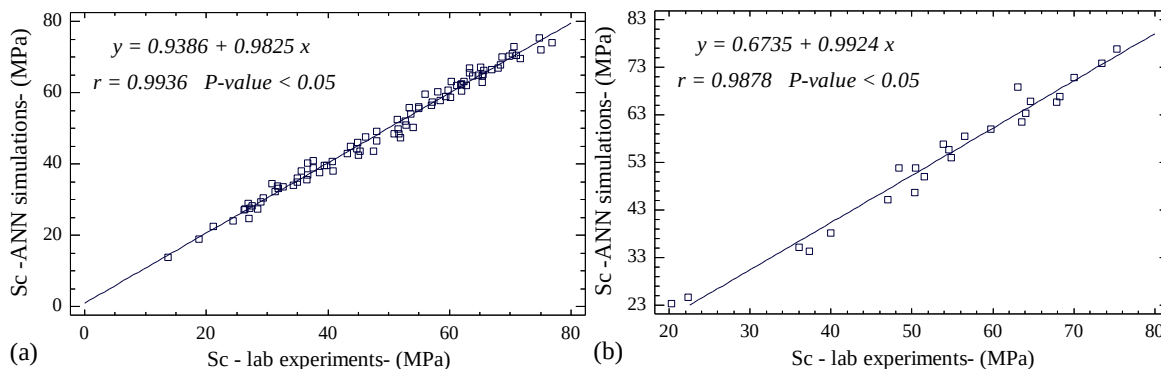


Figure 14. Scatter of actual values of concrete compressive strength and ANN simulated using BRA[12:3:1] (a) trained dataset (b) tested dataset.

3.2.3 Sensitivity Analysis for ANN models

As stated by Lee and Hsiung [65], a sensitivity analysis is required to identify those input variables that are important in contributing to the predicted output variable by each particular ANN model developed. In this study, the sensitivity analysis was based on Ref. [75], which is a connection weights and biases approach. In this method, the actual values of weights and biases between input vector-hidden layers and hidden layers-output layers are considered and the products across all the HN are added [56]. This approach provided explicit numerical (including signs) information on the

effect of each input variable on the output. Since the information is presented with the algebraic signs, the connection weight-bias approach permits the analyzer to know if the contribution was directly or inversely related to the output. The relative importance of the input variables related to the output variables is determined using Eq. (7) [76].

$$\beta_i = \frac{\sum_{j=1}^m w_{ij} w_{jk}}{\sum_{i=1}^n \sum_{j=1}^m w_{ij} w_{jk}} \quad (7)$$

For $i = 1, 2, 3, \dots, n$; $j = 1, 2, 3, \dots, m$

In this equation, β_i is the relative importance of i -th input variable, j is the index number of the HN, W_{ij} is the connection weight between the i -th input variable and j -th HN, and W_{jk} is the connection weight between the j -th HN and the k -th output node. Due to the random nature of the initial points of the searching algorithms, the ranking order was established based on the average of twelve simulations. These different arrays included both random initial points and random arrays among the training, validation, and testing datasets. Namely, each trained neural architecture was run from several random conditions, and the connected weights and biases were registered in Table 9. Even so, the net's architecture remained invariant as well as the number of training, validation, and testing points, which were fixed to be 75%, 5% and 20%, respectively, as stated above.

Once the sensitivity analysis was performed for each net's tested architecture, normalization of the

numbers based on the highest absolute value was performed. Finally, algebraic summation was carried out in order to rank the relative importance of each input variable (Table 9). Each ranking number is accompanied by the algebraic sign within parentheses after the Arabic number. This easily identifies the nature (directly or inversely) of the relationship between the input and output variables. Regardless of the algebraic sign, when the number increases, the relationship between both variables becomes less significant. Since the input variables are too many (twelve) and based on space considerations, only the contributions from the sensitivity analysis related to the nS, SF, and FA inputs will be analyzed because these variables are common to both the DOE analysis and the ANN simulations. Nonetheless, two controversial points occurred from the ANN analysis.

Table 9. Ranking order for input variables from sensitivity analysis on ANN simulations.

ANN model	nS (kg/m ³)	SF (kg/m ³)	FA (kg/m ³)	PC (kg/m ³)	WT (kg/m ³)	AG (kg/m ³)	SP (kg/m ³)	UW (kg/m ³)	AC (%)	FT (%)	IS (mm)	MA (day)
LM	5(+)	4(-)	2(-)	3(-)	6(+)	11(-)	7(-)	12(+)	10(-)	9(+)	8(-)	1(+)
BR	4(+)	6(-)	3(-)	5(-)	2(+)	12(-)	7(+)	11(+)	9(-)	10(+)	8(-)	1(+)

First, water content (WT) and Portland cement (PC) appeared to produce effects contrary to what one can expect in concrete technology (Table 9). This should be interpreted in relative terms since this study was developed at a fixed w/b = 0.35 with 24 different internal arrays of cementitious mixes (Table 3). It can be explained as follows. At long term, mixes such as {0.0:20:0.0} and {3.0:20:0.0} exhibited higher compressive strengths than the average value obtained by all the systems (Tables 10 and 11). In these mixes with high SF additions, the water requirement is elevated because of the high surface energy of the SF particles. Also, due to the high cement replacement levels, low amounts of PC are required. Therefore, these phenomena were captured by the ANN simulations, and the WT exhibits a positive contribution and the PC a negative contribution. Second, the LMBP revealed that the SP input variable had a negative contribution on compressive strength, whereas BRA exhibited the opposite behavior (Table 9). The SP amounts employed in the mix designs were found in

laboratory trials taken into account the maximum capacity of each system (mix design) before segregation or excessive bleeding were seen on any slump-cone or flow table test. However, the excess in SP content could not adversely affect the strength development at neither early nor later ages because the average strength rates for 3d/7d were 0.69 (LM) and 0.73(BR) and for 7d/28d were 0.74(LM) and 0.71(BR), as can be inferred from Tables 10 and 11, which are expected values. Then, from the point of view of concrete technology in systems with mineral additions these values are commonly found. The key point is that the amount of SP supported by FA systems is extremely small before segregation or bleeding is observed as compared to nS-systems. Considering the BRA, the explanation lies in the fact that additions of low calcium FA in the amounts used here (up to 40 wt%) showed good fluidity at the lowest SP contents employed, which is to be commonly expected. Also, from the present laboratory conditions and therefore from ANN simulations, FA-samples developed lower strength

(and strength gain) than plain, SF, and nS systems (Tables 10 and 11), as expected. Therefore, this phenomenon was easily detected by the trained net with architecture BR[12:3:1] showing the SP to be a positive influence on compressive strength. In this respect, ANN analysis by means of the BRA and the actual physical phenomenon agree. In contrast, the result obtained by LMBP algorithm is indicating the opposite behavior; SP increments tend to induce a deleterious effect on the compressive strength (Table 9). This output did not match the experimental conditions found by the authors. We will deal with this topic later in conjunction with the negative sign of the SF input variable captured by both algorithms (Table 9).

All the remaining signs and almost all the positions of the input variables were equally obtained by both algorithms (Table 9). The FA input variable was ranked at the second (LM) and third (BR) positions with negative contributions. This result agreed from DOE analysis (Table 4) where it is classified as significant for all ages and a negative contribution to the strength (p -value = 0.00). From a physical point of view, these results are expected. The nS content was the fourth (BR) and fifth (LM) variable, and its presence is related to compression strength gained. From DOE analysis (Table 4), the nS variable was also related to strength gain (p -value = 0.00); hence the results from ANN are justified. Again, from the concrete technology point of view, these results are expected.

In a similar fashion, the SF input variable was in the fourth (LM) and sixth (BR) ranking in the ANN analysis. This was the most difficult variable to interpret. As can be seen in Table 9, the SF variable was in higher positions (fourth and sixth) indicating a weak effect on strength as compared to nS and FA. This agrees with Table 4 from the DOE methodology where the strength contribution at the ages of 3, 7, and 28 days was not statistically significant (p -value ≥ 0.05). This was discussed in an early section of this document. Additionally, taking into account the negative sign, the SF variable contrarily to nS and FA input variables, the results from ANN algorithms do not coincide with the linear terms from the DOE analysis. At this respect, the authors propose two possible explanations: (i) since at early ages, i.e., up to 56 days, the strength rate development of the SF-systems was lower than both plain and nS-systems

(Tables 10 and 11), this could be successfully detected by both algorithms. (ii) A more rigorous analysis of DOE analysis (Table 4) reveals that statistically significant higher orders (interactive and quadratic terms) of the SF variable are mostly negative in nature rather than positive, which leads to a deleterious effect on the compressive strength (Table 4). According to the DOE analysis (Table 4), it should be noted, based on the p -value criterion, that the positive linear effect of the SF variable was statistically lesser influential than those observed for the negative nonlinear orders. In this sense, both the BRA and the LMBP showed a negative contribution of the SF on the compressive strength. These results could indicate that these two algorithms adapt better to the negative nonlinear orders of the SF variable rather than the positive linear effect. Nevertheless, while the BRA ranked the SF in the sixth position, the LMBP ranked the SF in the fourth position. Then, for this latter algorithm the role played by the SF variable was more important than that given by BRA. It could be attributed to the large HN present in the LMBP compared to the BRA. That is, the large number of HN in the LMBP tended to capture nonlinearities in the relationship of the variables. This second hypothesis could be also related to the negative behavior of the SP in the LMBP algorithm. From a physical point of view, the authors have reported in other publications [77][78] that a predominant nonlinear effect occurs in the rheological behavior resulting from the simultaneous use of the SP and nS/SF in some cementitious systems.

According to the DOE methodology (Table 4), the LOF condition appeared 100% of the time. This is related to the fact that from ANN sensitivity analysis the nS, SF, and FA inputs were not necessarily the most important contributing variables to compressive strength. LMBP registered the PC input variable as being more significant than SF and nS (Table 9), while BRA showed that the WT input variable was more important than the FA, nS, and SF variables. This analysis takes into account that, in the DOE analysis, the nS, SF, and FA are the only input variables used for the mathematical models. Also, from Table 9 it is seen that the input variable MA (maturity age) had the highest positive contribution in both algorithms. This result is expected because the hydration and pozzolanic reactions are time dependent. Nevertheless, this important (the most significant)

input variable was not considered, since by technical considerations the ANN simulations were conducted using all the data at all ages while the DOE analysis was performed at specific ages of 3, 7, 28, 56, and 90 days. Therefore, for the present experimental and computational research work, it can be argued that

statistical analysis in conjunction with ANN simulations with an adequate sensitivity analysis, effectively improved the understanding of the system's overall behaviors.

Table 10. Comparison of results in compression between actual and simulated values from ANN using LMBP [12:15:1].

Mix proportions* {nS:SF:FA}	3 days Actual	3 days ANN	7 days Actual	7 days ANN	28 days Actual	28 days ANN	56 days Actual	56 days ANN	90 days Actual	90 days ANN
{0.0:0.0:0.0}	24.37	23.52	31.90	34.27	50.30	45.58	52.84	50.46	54.91	55.71
{3.0:0.0:0.0}	36.68	38.26	54.06	53.56	67.84	67.57	70.95	70.26	74.81	72.94
{6.0:0.0:0.0}	30.84	31.61	51.98	49.95	65.13	67.10	70.39	69.88	73.48	72.66
{0.0:0.0:20}	22.90	20.97	29.39	30.55	43.70	42.85	51.51	48.94	54.92	54.71
{0.0:0.0:40}	13.75	13.45	20.29	23.88	35.62	37.19	43.25	43.68	51.65	49.90
{3.0:0.0:40}	18.74	18.90	28.99	28.93	40.78	39.99	44.90	45.27	50.46	51.18
{3.0:0.0:20}	27.58	28.00	38.68	39.37	52.70	51.29	53.91	56.24	61.25	61.68
{6.0:0.0:40}	26.31	26.83	36.00	36.20	46.19	46.37	51.67	51.56	58.53	57.74
{6.0:0.0:20}	35.01	34.59	45.04	44.53	54.83	54.93	60.13	59.49	62.36	64.48
{0.0:10:0.0}	26.29	26.40	40.84	40.22	56.16	56.06	59.78	61.39	65.42	65.67
{0.0:20:0.0}	29.02	29.46	45.31	44.48	63.28	64.15	75.09	73.65	75.29	78.31
{3.0:20:0.0}	31.37	32.20	46.98	45.96	63.36	64.18	68.71	71.61	76.85	75.43
{3.0:10:0.0}	34.94	35.55	47.97	48.65	62.72	62.50	66.96	66.58	70.01	69.99
{6.0:20:0.0}	36.65	36.37	50.89	49.66	64.67	64.92	71.65	69.61	70.63	72.81
{6.0:10:0.0}	37.64	38.44	51.50	49.95	60.30	61.77	68.29	65.56	69.78	69.09
{1.5:0.0:10}	26.96	24.63	37.27	36.58	47.97	48.94	53.67	53.66	55.97	58.61
{0.0:10:20}	21.08	20.63	34.34	34.02	48.40	50.66	58.74	57.13	61.85	62.13
{0.0:5.0:10}	28.43	27.05	37.61	39.17	56.99	55.28	63.52	62.08	65.71	66.90
{1.5:5.0:0.0}	31.71	31.08	44.80	45.15	58.14	59.62	63.83	63.86	63.08	67.78
{1.5:10:10}	27.10	27.75	39.79	38.95	56.50	55.58	65.44	63.82	68.00	68.92
{1.5:5.0:10}	26.86	27.77	39.35	40.76	54.57	54.91	61.99	59.85	64.80	64.41
{1.5:5.0:20}	22.36	24.36	36.56	37.12	51.48	51.58	57.16	57.04	61.97	62.07
{3.0:5.0:10}	32.67	32.69	47.44	45.99	59.41	59.75	64.09	64.09	68.41	68.21
{3.0:10:20}	24.96	25.92	39.92	38.35	53.39	54.14	59.74	60.51	65.46	65.37

* Mix proportions expressed as percentage of cementitious materials.

Table 11. Comparison of results in compression between actual and simulated values from ANN using BRA [12:3:1].

Mix proportions* {nS:SF:FA}	3 days Actual	3 days ANN	7 days Actual	7 days ANN	28 days Actual	28 days ANN	56 days Actual	56 days ANN	90 days Actual	90 days ANN
{0.0:0.0:0.0}	24.37	23.99	31.90	33.13	50.30	46.67	52.84	50.95	54.91	56.10
{3.0:0.0:0.0}	36.68	40.33	54.06	50.33	67.84	65.64	70.95	70.44	74.81	75.41
{6.0:0.0:0.0}	30.84	34.52	51.98	47.36	65.13	67.19	70.39	70.87	73.48	73.90
{0.0:0.0:20}	22.90	21.04	29.39	30.34	43.70	44.80	51.51	50.05	54.92	55.66
{0.0:0.0:40}	13.75	13.85	20.29	23.39	35.62	37.91	43.25	42.84	51.65	48.55
{3.0:0.0:40}	18.74	19.00	28.99	27.41	40.78	40.59	44.90	45.94	50.46	51.81
{3.0:0.0:20}	27.58	28.21	38.68	37.57	52.70	52.01	53.91	56.92	61.25	61.91
{6.0:0.0:40}	26.31	27.27	36.00	35.13	46.19	47.49	51.67	52.56	58.53	57.85
{6.0:0.0:20}	35.01	34.84	45.04	42.38	54.83	54.07	60.13	58.62	62.36	63.18
{0.0:10:0.0}	26.29	27.10	40.84	38.09	56.16	55.09	59.78	59.95	65.42	64.72
{0.0:20:0.0}	29.02	29.35	45.31	43.62	63.28	66.99	75.09	72.05	75.29	76.82
{3.0:20:0.0}	31.37	32.28	46.98	45.24	63.36	65.65	68.71	70.09	76.85	74.07
{3.0:10:0.0}	34.94	36.09	47.97	46.35	62.72	61.98	66.96	66.45	70.01	70.76
{6.0:20:0.0}	36.65	36.86	50.89	48.37	64.67	65.80	71.65	69.61	70.63	72.93
{6.0:10:0.0}	37.64	40.82	51.50	49.81	60.30	63.15	68.29	66.89	69.78	70.33
{1.5:0.0:10}	26.96	24.73	37.27	34.32	47.97	49.07	53.67	54.10	55.97	59.57
{0.0:10:20}	21.08	22.50	34.34	34.05	48.40	51.89	58.74	56.78	61.85	62.19
{0.0:5.0:10}	28.43	27.36	37.61	38.78	56.99	56.53	63.52	61.42	65.71	66.25
{1.5:5.0:0.0}	31.71	33.79	44.80	44.23	58.14	60.14	63.83	64.57	63.08	68.79
{1.5:10:10}	27.10	27.51	39.79	39.62	56.50	58.42	65.44	62.85	68.00	66.86
{1.5:5.0:10}	26.86	28.94	39.35	39.45	54.57	55.62	61.99	60.34	64.80	64.94
{1.5:5.0:20}	22.36	24.69	36.56	35.55	51.48	52.42	57.16	57.43	61.97	62.47
{3.0:5.0:10}	32.67	33.45	47.44	43.49	59.41	58.81	64.09	63.34	68.41	67.73
{3.0:10:20}	24.96	26.70	39.92	38.12	53.39	55.84	59.74	60.60	65.46	65.16

* Mix proportions expressed as percentage of cementitious materials.

4. CONCLUSIONS

The purpose of this study was to analyze the compressive strength of plain, binary, ternary, and quaternary concrete samples containing low calcium fly ash (FA), micro- (SF) and nano-silica (nS) additions in the presence of a superplasticizer (SP). The numerical analyses were conducted using both statistical design of experiments (DOEs) and artificial neural networks (ANNs) methodology. The mechanical properties were analyzed at 3, 7, 28, 56,

and 90 days of maturity. The principal results can be summarized as follows:

- The simultaneous used of SF and nS additions in concrete induced a pronounced nonlinear effect on the compressive strength response variable. Also, the curvature exhibited by the response surfaces continuously switched from positive to negative. This complex behavior could induce the lack-of-fit of the second-order model presented in the DOEs with nS, SF, and FA as

inputs. Nevertheless, another explanation on the lack-of-fit can be inferred from the ANN sensitivity analysis, which showed that nS, SF, and FA were not necessarily the most important variables contributing to the compressive strength.

- For compression strength analysis, the replacement of cement by either SF or nS particles could effectively improve the strength gain with respect to the control system. This is attributed to the pozzolanic reaction between the amorphous SiO_2 and the Ca(OH)_2 present in hydrated cement. In addition, the higher mechanical performance obtained from the addition of the nano-silica particles compared to silica fume addition was statistically demonstrated by both the DOE analysis and ANN models.
- For the present experimental conditions of w/b, age of testing, quality of FA and proportions, the combined use of nS and FA was not acceptable. Even at the high level of 6.0 wt%, the presence of nS did not compensate for the strength loss induced by the FA additions. All the interactions between the nS with the FA additions exhibited a negative effect as seen in the DOEs. This conclusion is of extreme importance for concrete technology because the properties of nS, such as its high surface energy and therefore, its high reactivity, could be of interest in mixes with low cement and/or low amorphous silica contents that is typical in some systems with high FA additions (i.e., high-volume fly ash concrete). This important phenomenon was correlated with another research carried out on nS and FA [62], where due to the presence of the highly reactive nS particles the pozzolanic effect of FA was jeopardized.
- The trained ANN models were utilized to study the effects of mix proportions of cementitious materials on compressive strength at several ages of testing. The input variables used for the development of the ANN models were the amounts of nS, SF, FA, Portland cement, added water, aggregates and the SP. Also, air content, flow area from the flow table test, initial slump, and the unit weight in the fresh state were used as input variables. From the results, it is possible to conclude that, in the present work, ANN simulations were suitable computer tools and can

adequately predict the compressive strength behavior of ternary and quaternary concrete mixes with values being very close to the experimental data.

- The general results from response surface analysis of the design of experiments indicated that, in the developing of the second-order polynomial models, the analysis of variance showed that the most important parameters influencing compressive strength (both positive and negative) were the linear terms of nS and FA and the interaction terms nS•SF and nS•FA. These behaviors were also observed by means of two independent algorithms using ANN simulations.
- In addition to the typical training and testing datasets, the results of the adjusting and predictive capabilities of the ANN models were also compared with those obtained by using fifteen simultaneous designs of experiments through the ages of analysis. In conclusion, excellent performance and good generalization were achieved with the performance of the ANN models being better than that from the design of experiments. Additionally, based on the sensitivity analysis of the ANN models, a physical explanation to the lack-of-fit condition experienced by the design of experiments was provided. In closing, for the present experimental and computational research work, it can be concluded that DOE methodology in conjunction with ANN simulations and an adequate ANN-sensitivity analysis effectively improved the mathematical and physical understanding of the system's overall behaviors.

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RESUMEN

El presente documento establece las instrucciones detalladas para la preparación del manuscrito para arbitraje en la Revista Latinoamericana de Metalurgia y Materiales (RLMM). El Resumen no debe ser mayor a 300 palabras.

Palabras Claves: Instrucciones para autor, Formato, Plantilla MS-Word, Estilos.

TITLE OF THE MANUSCRIPT

ABSTRACT

The present document presents the detailed instructions for the edition of the manuscripts submitted to the Revista Latinoamericana de Metalurgia y Materiales (RLMM). The abstract should be no longer than 300 words.

Keywords: Guide for Authors, Format, MS-Word Template, Styles.

1.- INTRODUCCIÓN

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Completado este proceso, los autores recibirán un correo de aceptación, por parte del respectivo Editor de Área, donde se indicará, de ser factible, el volumen en el cual será publicado su trabajo, realizándose primeramente una publicación "on-line" del trabajo antes de su aparición en la versión impresa de la revista.

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Márgenes de 2,00 cm por cada lado, excepto el superior que debe ser de 2,50 cm, en papel tamaño carta.

Usar letra Times New Roman y escribir todo el texto a espacio simple. Los artículos pueden ser escritos en español, portugués o inglés.

La primera página del manuscrito debe contener: título del trabajo, autores, afiliación y dirección, correo electrónico del autor "a quien corresponda", resumen y palabras claves, tal y como se ejemplifica en el inicio de este documento.

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Debajo de la afiliación, colocar el correo electrónico del autor de correspondencia (corresponding author). Identificar con un asterisco en la línea de autores el nombre del autor o autores a quienes pertenecen los correos electrónicos (máximo dos autores).

El resumen del trabajo no debe ser mayor de 300 palabras escrito en dos de los idiomas mencionados, correspondiendo el primer resumen al idioma usado para el manuscrito (ej. español e inglés o portugués e inglés). Una lista de 3-4 palabras claves debe aparecer a continuación de cada resumen en los idiomas seleccionados.

Antes del texto de resumen, debe colocarse la palabra "Resumen" o "Abstract" en el formato mostrado, según sea el caso. En la siguiente línea iniciar el texto del resumen con un párrafo justificado. Luego del texto del resumen, colocar las palabras claves, en *itálicas* tal y como se muestra en esta plantilla.

2.1.- Texto principal

Todo el texto debe ser escrito en tamaño 11, párrafos justificados y sin sangría, con un espaciado entre párrafo de 4 pts, a excepción de los espaciados entre párrafos y títulos o subtítulos que se indican en la siguiente sección.

Toda abreviatura, acrónimo y símbolo debe ser definido en el texto en el momento que es presentado por primera vez.

2.1.1.- Títulos

Todos los títulos de las secciones principales (títulos de 1 nivel) serán numerados con números arábigos, a saber: 1. Introducción, 2. Parte Experimental, 3. Resultados y Discusión, 4. Conclusiones, 5. Agradecimientos y 6. Referencias. Deben estar en negritas, mayúsculas, tamaño 11, alineados a la izquierda.

Títulos de 2 niveles (Ej. 3.1 Materiales, 3.2 Ensayos, etc.) deben estar en negritas, minúsculas con la primera letra en mayúscula, alineados a la izquierda, con el color indicado.

Subtítulo de Tercer Nivel (Ej. 3.2.1 Análisis Térmico, 3.2.2 Análisis Morfológico, etc.), deben estar en itálicas sin negrita, minúsculas con la primera letra en mayúscula, justificados.

3.- RESULTADOS Y ANÁLISIS DE RESULTADOS

3.1.- Figuras y Tablas

Los autores deben ubicar las Figuras y Tablas inmediatamente después de ser citadas en el texto, tal y como desean que aparezcan en la versión final del artículo y centradas. Se recomienda que las figuras y tablas ocupen un ancho máximo de 8,00cm, ya que será ubicadas en un formato de 2 columnas al momento de la diagramación final del artículo aceptado para su publicación.

Las figuras deben presentar sus respectivos títulos en tamaño 10 y numerados con números arábigos de acuerdo a orden de aparición, ubicado en la parte inferior para las figuras (ver Figura 1). Similarmente en el caso de las tablas, pero colocando el título en la parte superior de ésta. El tamaño de letra de los rótulos, leyendas, escala y títulos de ejes de las figuras, deben estar entre 10-11 pts una vez definido el tamaño definitivo.

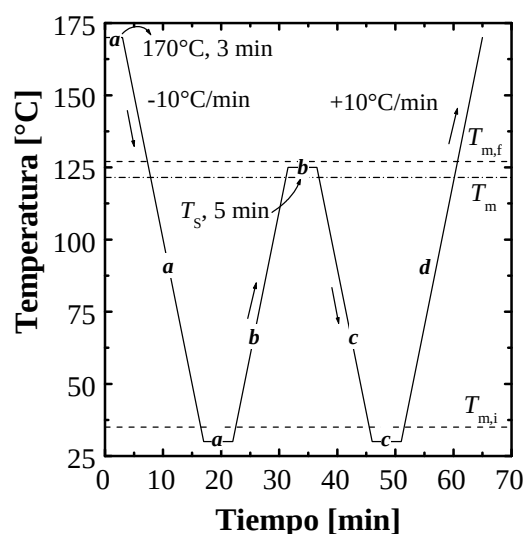


Figura 1. Tratamiento térmico de autonucleación aplicado en un equipo DSC a un PELBD.

En las tablas (ver Tabla 1), el encabezado de las columnas debe ir en itálica y en tamaño 10, el texto restante de la tabla en igual tamaño y sin itálica (incluyendo título de la tabla), y las notas al pie de tabla en tamaño 9. Igualmente numeradas por orden de aparición.

Tabla 1. Características de las resinas de PET empleados en el trabajo.

Propiedades	PET-1	PET-2	PET-3
Tipo	Copol.	Copol.	Homopol.
Contenido de ácido isoftálico [% mol] ^a	2,32	2,28	-
Contenido de dietilenglicol [% mol] ^a	2,57	2,52	1,85

a: Determinación realizada por Resonancia Magnética Nuclear de protones (RMN-H1) en solución.

No se deben usar líneas verticales para definir columnas. Sólo se permite el uso de líneas horizontales, trazándose al menos 3 líneas con el ancho de la tabla que delimite el alto de la misma y que separe el encabezamiento de las columnas del resto del texto de la tabla (ver Tabla 1).

Se prefiere el uso del sistema de unidades SI. Si el texto es escrito en español o portugués, usar como separador decimal la “coma” y no el “punto”.

Cuidar la resolución de las figuras u objetos para garantizar su calidad al visualizar en pantalla e imprimir. Para las fotos se recomienda una resolución igual o superior a 300 dpi, y que las mismas sean insertadas a partir de archivos de imágenes con los siguientes formatos JPG, GIF o TIF (*evitar el formato BMP*).

En las figuras se debe cuidar el grosor de los ejes y trazados de curvas (superior a 0,5 pto), así como tamaño de los símbolos (igual o superior a 7 pto). Se debe evitar la presentación de figuras obtenidas por digitalización vía escáner, ya que puede traer problemas de calidad.

Colocar las figuras, fotos u otros objetos desvinculados de los programas que le dieron origen, lo cual permite un archivo con un menor tamaño y minimizar los riesgos de alguna modificación involuntaria de su contenido.

En la elaboración de figuras o ilustraciones es recomendable **no editar** usando las opciones de dibujo que ofrece el MS-Word. Si se hace, se sugiere al final agrupar todos los elementos que forman la figura y hacer un “copiado y pegado especial” como imagen en el mismo programa y colocar en “línea con el texto” lo cual evita que la figura flote y se desplace del lugar deseado en el texto (para esto último, hacer clic en la figura y seleccionar en el menú Formato, la opción “Imagen...” e ingresar a la ficha “Diseño”). De no seguirse las recomendaciones anteriores, no hay garantía de conservar la edición realizada a la figura, durante los ajustes finales de formato que requiera realizar el equipo de trabajo de la revista.

En caso de que las figuras contengan elementos a color, sólo se garantizan los mismos en la visualización digital del artículo, más no en la reproducción del número impreso cuando salga en circulación, por lo que se recomienda usar colores que sean emulados en una escala de grises que permita su distinción al imprimir en calidad láser en blanco y negro.

3.2.- Ecuaciones y estructuras químicas

Las estructuras químicas deben ser editadas con el uso de algún programa adecuado de dibujo para tales fines.

3.2.1.- Ecuaciones

Van centradas en la columna, identificadas con un número entre paréntesis numerando de forma correlativa desde 1 a medida que aparecen en el texto:

$$F = m \cdot a \quad (1)$$

Se debe definir con claridad el nombre de cada una de las variables que constituyen la ecuación y se prefiere el uso de exponentes fraccionarios para evitar el símbolo de raíz. Cuidar que el tamaño de las letras y símbolo no sea superior a 11 pto.

4.- CONCLUSIONES

Ingresar las conclusiones del trabajo en formato de párrafos. Evitar conclusiones largas y el uso de viñetas.

5.- AGRADECIMIENTOS

Colocar agradecimiento de ser necesario. Esta sección es opcional.

6.- REFERENCIAS

Cuando la cita implique la conveniencia de mencionar el nombre del autor o autores, indicar con un número arábigo entre corchete en línea con el texto antecedido por el apellido o apellido según los casos siguientes:

Un autor (Ej. Pérez [1] evaluó los...)

Dos autores (Ej. Liu y Gómez [2] evaluaron los...)

Más de dos autores: Indicar sólo el apellido del primer autor seguido de término latín “et al.” en itálica (Ej. Pérez et al. [3] evaluaron los...).

Cuando la cita corresponde a un concepto general, fundamento, planteamiento, etc., que no requiere la mención al autor o autores, la cita se hace usando sólo el número entre corchete al final de la idea (típicamente al final de una oración o párrafo).

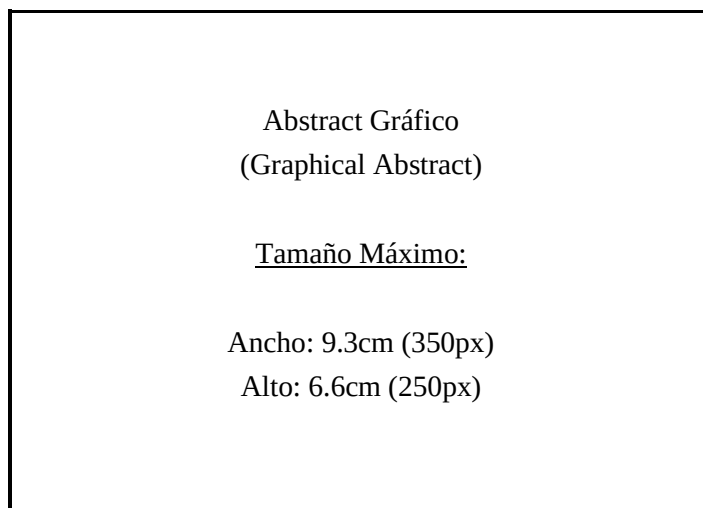
En el caso de una figura tomada sin modificación alguna de un trabajo ya publicado, no es suficiente con citar una referencia, ya que se puede estar violando “Derechos de Autor” (este es particularmente importante en caso de que la fuente bibliográfica sea un artículo científico). Es necesario que el título de la figura haga mención al “permiso de reproducción” otorgado por la editorial responsable de la publicación de donde se ha tomado la cita, permiso el cual debió ser oportunamente gestionado por los autores del manuscrito a ser remitido a la RLMM.

Seguir el formato indicado a continuación de acuerdo al tipo de referencia a:

- [1]. Fillon B, Wittman JC, Lotz B, Thierry A. J. Polym. Sci. B: Polym. Phys. 1993; 31 (10): 1383-1393.
- [2]. Brydson JA. *Plastics Materials*, 7ma Ed. Oxford (Inglaterra): Butterworth Heinemann Ltd., 1999, p. 151-159 (o Cap. 1, según convenga).
- [3]. Yoshimura M, Suda H, “Hydrothermal Processing of Hydroxyapatite: Past, Present, and Future”. En: Brown PW, Constantz B (eds.), *Hydroxyapatite and Related Compounds*. Boca Raton (EE.UU.): CRC Press Inc., 1994, p. 45-72.
- [4]. Zhang M, Huang J, Lynch DT, Wanke S, “Calibration of Fractionated Differential Scanning Calorimetry Through Temperature Rising Elution Fraction”. En: *Proceedings del 56th Annual SPE Technical Conference (ANTEC) 1998*. Georgia (EE.UU.): Society of Plastics Engineers, 1998, p. 2000-2003.
- [5]. Santana OO. *Estudio de las Fractura de Mezclas de Policarbonato con Acrilonitrilo-Butadieno-Estireno*, Tesis Ph.D. Barcelona (España): Universitat Politècnica de Catalunya, 1997.
- [6]. Norma ASTM D 790-02, *Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials*, Vol. 8.01, Filadelfia (EE.UU.): American Society for Testing and Materials, 2003.
- [7]. Takahashi M, Adachi K, Menchavez RL, Fuji M, J, *Mat. Sci.* 2006 [On-Line]; 41 (7): 1965 – 1972 [citado 10-May-2006]. ISSN (on-line): 1573-4803
- [8]. Othmer K. *Encyclopedia of Chemical Technology* [en línea]. 3rd ed. New York: John Wiley, 1984 [citado 3-ene-1990]. Disponible a través de: DIALOG Information Services, Palo Alto (California, USA).

Resumen Gráfico (Graphical Abstract)

Para la versión online de la RLMM, se les pide a los autores que incorporen un Resumen Gráfico (Graphical Abstract) de su trabajo. Este resumen gráfico debe ser: una figura original (no utilizada en su totalidad en la escritura del manuscrito), a color, cuyo tamaño horizontal esté entre 300 a 350px (7.9 a 9.3cm), y con un tamaño vertical entre 200 a 250px (5.3 a 6.6cm). Se les invita a los autores a visitar los últimos números de la RLMM, donde podrán observar diferentes tipos y modelos de resúmenes gráficos.



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Para la versión sometida a arbitraje, el Autor de Correspondencia DEBERÁ remitir vía la página web: www.rlmm.org (previo registro como usuario) su manuscrito en formato .PDF (siguiendo las instrucciones según esta plantilla). Adicionalmente es OBLIGATORIO que el Autor ingrese todos los autores del manuscrito (llenando todos los campos requeridos por el sistema por cada autor adicional), y que de igual forma anexe la lista de sugerencias de posibles árbitros para su trabajo como "Archivo Adicional" utilizando la planilla titulada "RLMM-PostulacionArbitros.doc", que puede ser descarga de la página web de la revista.

Mientras el proceso de Arbitraje esté en curso, todas las versiones corregidas del manuscrito deberán ser enviadas en formato .PDF; si el manuscrito es aceptado para su publicación en la RLMM, el Editor o el Editor de Sección de turno se comunicará con el Autor de Correspondencia para pedirle la versión final aceptada del manuscrito en formato .DOC (la cual será utilizada para el proceso de diagramación final) y cualquier otro archivo adicional, tal como la planilla de "Transferencia de Copyright".

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Asimismo, es importante para el Comité Editorial de la **RLMM** reducir el tiempo dedicado a las actividades de edición (formato) del manuscrito. Por esta razón es necesario que los autores hagan uso de las instrucciones de formato indicadas en la siguiente sub-sección, a fin de poder difundir en versión electrónica el artículo en su versión final (revisada) en un plazo de tres (3) meses, a partir de la fecha de envío a los autores de las observaciones realizadas por los árbitros y por el propio Comité Editorial.

Completado este proceso, los autores recibirán la carta/e-mail de aceptación definitiva donde se podrá indicar el volumen en el cual será publicado su trabajo, realizándose primeramente una publicación "on-line" del trabajo antes de su aparición en la versión impresa de la revista.

3. INDEXACIÓN

La **RLMM** se encuentra indexada en las siguientes bases de datos e índices bibliográficos:

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- CSA Engineering Research Database: Incluida en los siguientes índices:
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- CSA High Technology Research Database with Aerospace: Incluida en los siguiente índices:
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De interés para investigadores venezolanos:

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