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RESEARCH ARTICLE

UPGRADING OF CALCIUM SULFATE USING A SUPERCRITICAL CO_2 BRAYTON CYCLE COUPLED TO CONCENTRATING SOLAR POWER: TEMPERATURE-REDUCING DECOMPOSITION

A. Beyoud and A. Bouhaouss
Laboratory of Nano Structures, Process Engineering and Environment, Faculty of Sciences, Mohammed V University, Ibn Battouta Avenue, Agdal - Rabat, Morocco.

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Abstract

The decomposition temperature of $CaSO_4$ slag is very high. There is no temperature limit to using supercritical carbon dioxide to lift it from the solar field to the decomposing waste reactor. However, the higher the temperature, the more the losses by radiation are. The situation makes the use of solar resources difficult or even impossible. Therefore, a reaction medium containing calcium chloride and some precursors was proposed. Feasibility and products predictions were performed by the thermodynamic studies, the thermogravimetric technique analysis, and the X-ray diffraction verification. Consequently, the pyrometallurgical process based on the treatment of mixtures of $CaSO_4$ with carbon or silica show reacts at temperatures achievable with renewable energies, which are evaluated by thermogravimetric analysis from respectively 500°C and 750°C. On the other hand, the outcomes of XRD analysis give an RIR rate of calcium sulfide (CaS) of about 33% (27% with silica). Therefore, the (CaS) compound leads smoothly to sulfur dioxide used in the electrolysis process. Therefore, sulfuric acid and hydrogen are usual value-added products from Westinghouse electrolysis. Indeed 1/3 of the sulfuric acid produced helps generate H2S, and finally, the elemental sulfur will yield spontaneously.

Introduction:-

Although Morocco has taken a strong initiative to develop renewable energies since 2008 in order to cope with high levels of energy imports and reduce its dependence on fossil fuels, it was able to reach 77th place on the index. Energy Trilemma of the Year 2017, after ten years (2008-2017), these results are still alarming in terms of energy security; however, the results of energy equity and energy sustainability are hardly acceptable [1]. Solar technology can play a key role in improving energy security and sustainability like other countries considered producing oil in Africa [2, 3]. On the other hand, in the sustainability point of view, the slag, a mixture of molten ash, comes from metallurgical industries or power stations, with metallurgical plants producing an average of 523.10^{9}kg of slag per year worldwide [4-5]. The recovery of this industrial waste consists of the generation of value-added products by different approaches: the decomposition of the constituents of the waste, in order to retain the gases or recover valuable chemical materials, the recycling of the waste heat in these industries by processes [6,7]. For example, research has developed a process for producing hydrogen from steel slag, because increasing the weight of the slag by blowing the gas ArH_2O causes the oxidation FeO present in the slag at Fe_2O_3 and the analysis of the exhaust gases by a quadrupole mass spectrometer reveals the generation of hydrogen gas[8].In this contexte, when producing

Corresponding Author:- Abdelkader Beyoud
Address:- Laboratory of Nano Structures, Process Engineering and Environment, Faculty of Sciences, Mohammed V University, Ibn Battouta Avenue, Agdal - Rabat, Morocco.

hydrogen by conventional energy resources, it considered an energy carrier. However, it is green energy, in case the renewable energies generated it. Most importantly, the combination of useful and pleasant, and the use of renewable energies along with waste recycling. Indeed, the water molecule dissociation is very expensive energetically. On the other hand, this water dissociation implies introducing several thermochemical processes among the sulfur cycles there, is the hybrid sulfur cycle, the sulfur iodine cycle, the bromine cycle sulfur, and the sulfur ammonia cycle, and so on. They are the most advanced in green hydrogen production technology. Regarding the sulfur cycles, the sulfur-iodine cycle (SIC) considered a process with reduced electricity consumption if all the reagents of the cycle are in gaseous or liquid form according to the Japan Atomic Energy Agency « JAEA» [9]. Researchers have also reported that some aspects are necessary for the upgrade; in particular, the cycle temperature must exceed 800°C to reach 950°C [9]–[11]. The proposition motivated by the acceptable reaction kinetics and the compensated thermal losses. The Hybrid Sulfur Cycle (HSC) is a version of SIC. It operates at around a temperature of 800°C, where additional power is required for the electrolysis step. This process allows one-third (1/3) of the electrical power to supply to the direct water electrolysis [12]. Recently, various configurations studied for maximum temperatures to be as low as possible. On the other hand, the Westinghouse process is one of the sulfur cycles providing appropriate operating conditions [13]. The Ispra Mark (Westinghouse cycle) uses sulfur dioxide for aiding water electrolysis, at a low temperature [80-120] °C, with very little heat input [13]. This process produces hydrogen and sulfuric acid at the end of the process. However, it does not explain how to recycle sulfuric acid to regenerate sulfur dioxide. However, sulfuric acid is highly demanded by the phosphate industry because the production of sulfuric acid is energy-intensive. It costs around 30kJ/mol in its electrical form input at a high temperature of 950°C and in a catalytic medium of vanadium pentoxide [14].

The background review carry out widlythe calcium sulfate dissociation. Moreover, the energy intake is very varied with utterly high temperatures [15]–[23, 24]. This work involving the retention of elemental sulfur and its easily exploitable gaseous derivatives presents a range of conclusive and promising results at temperature accessible by solar energy technology. Thecalcium sulfate has some specific features leading to use its derivatives as adjuvants such as limestone or lime for decreasing temperature decomoposition [25]. In general, these introduced to dissociate the sulfate and recover the sulfur products useful for the chemical technologies. Most of the work discusses the dissociation of calcium sulfates at very high temperatures and the introduction of metal oxide builders [15]–[17], [26], and [27]. The reduction of calcium sulfate $CaSO_4$ in a reducing atmosphere of carbon monoxide gas is spontaneous. The objective of the production of calcium sulfide (CaS) is to reduce the decomposition temperature. CaS is easily used in the process of producing sulfur dioxide with an absorbent buffer solution, which forms with potassium citrate[28], [29].

Furthermore, solar energy extends to the thermochemical process. In this case, researchers examined the Brayton cycle coupled with a two-step thermochemical cycle based on redox reactions. Co_3O_4/CoO. [30].The retention of the basic components of the slag requires a supply of thermal energy at a very high temperature, so it is not economically advantageous to decompose this residue with solarenergy resources. Consequently, this work proposes to lower the decomposition temperature of calcium sulfate, the recovery of sulfur or its derivatives for the possible treatment in reactors thermally coupled par extrapolation to a concentrating solar power via Brayton cycle, to produce hydrogen and sulfuric acid. The why we will take up this challenge and introduce precursors to lower the decomposition temperature of commercial calcium sulfate hemihydrate (From now on called HDH) to temperatures accessible from concentrated solar énergy. ATG, DTG, and DRX will carry out a posteriori. Parallelly, the prediction of the reactions must precede a thermodynamic study.

Principle and processes:-

HDH recycling principle and its future extrapolating system:

The process revolves around two main axes:

1. Axis of dissociation of the HDH molecule that allows the recovery of sulfur or its derivatives
2. Axis of Westinghouse electrolysis, which is a two-step hybrid electrolytic process for breaking down the water molecule

The sulfur dioxide gas retained by HDH will be used in this sub-process, the reaction of which indicated by equation (Eq.1) is the overall reaction that requires an input of energy (thermal and electrical) ΔrH = 88 kJ / mol, over a range temperature [80 120] °C.

$$SO_2(aq) + 2H_2O(l/g) \rightarrow H_2(g) + H_2SO_4(aq) \quad \text{(Eq.1)}$$

$$M\left(H_2\right)=\frac{\eta_{(bs)}.\eta_{(elec)}.\eta_{(ELZ)}.Q_{REG,bs}}{HHV} \quad \text{(Eq.2)}$$

With $M\left(H_2\right)$, HHV = 39 kWh / kgH_2 and $Q_{(REG,bs)}$ are the mass of hydrogen produced, the higher calorific value of hydrogen, and the amount of heat regenerated respectively, in addition, the thermal efficiency in the secondary loop of the SBC $\eta_{(bs)}$, the electrical conversion efficiency $\eta_{(elec)}$, and the electrolysis efficiency $\eta_{(ELZ)}$. The Brayton thermodynamic cycle is the future conversion of concentrated solar energy and delivers both thermal and electrical sources, which thus, couple downstream to thermochemical and electrolytic reactors as showen in Fig. 1.

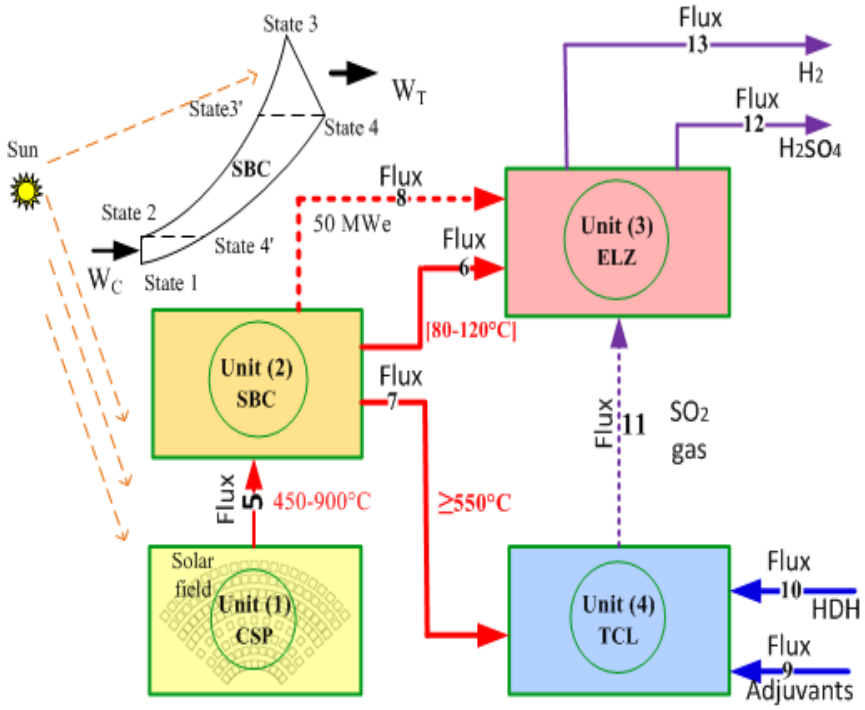


Figure 1:- The industrial conception process for upgrading HDH to produce Hydrogen and Sulfuric acid.

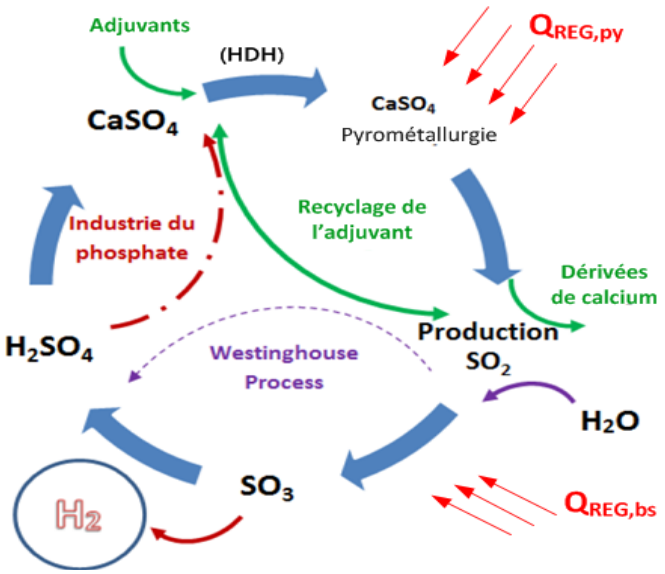


Figure 2:- Schematic diagram of the coupling of a power supply upstream of a solar field and downstream of two operating units, one thermochemical and the other electrolytic.

HDH and adjuvants mixed in the unit operation of thermochemical reactor at an acceptable temperature allow the recovery of one of the sulfur derivatives. Valuable sulfur dioxide gas demanded the Ispra Mark electrolytic reactor unit operation. (Westinghouse process), for the production of hydrogen and sulfuric acid.

Fig. 1 shows the heart of the HDH upgrade process, where the unit (2) is the Brayton cycle of supercritical carbon dioxide (SBC). The last process described in our preview work [31]. Thus, the secondary loop used the distribution heat between the different operating units, such as the chemical reactors: the electrolytical reactor unit (3), and the thermochemical unit (4). Whereas theunit (1) denotes the solar field feeding heat to the receptor combustor of the SBC.Fig. 2 presents the industrial conception for upgrading the HDH composing of ($CaSO_4.0.5H_2O$) and adjuvants, introduced in the operating unit of the thermochemical reactor. The last receives the heat from the fraction of heat, generally, the excessed solar heat over the design point, the transfer made by the supercritical carbon dioxide (sCO_2), represented by the flux 7 in the figure 1 at the temperature up to 550°C between the unit (2) and (4).

Flux (11) contains sulfur dioxide gas coming from the sulfur derivatives products in the unit (4), with the hot water highlighted by flux (6) coming from the cooling phase of the Brayton cycle between state (4') and state (1), making the feed of electrolysis in the operating unit (3). The flux (8) represents the electric power supply to this unit (ELZ).

Approaches to the process of thermochemical reactions

Means of thermodynamic analysis: Thermo-physical data of chemical compounds

Beforehand, the calculations use the databases of the software FactsSageV8 (educational version). This application provides data for certain thermophysical properties, such as specific state functions (Enthalpy, entropy, free enthalpy, and so). It collects the values required by the FToxid, FactPS, and FTsalt database implemented in the mentioned software. A sample data compared with the standardized base NIST showed an excellent correlation [32]. The choice of this comparison reference NIST recommended strongly by experts [33-35], where a high quality and accuracy data drive them.

Reagents and materials used and analyzed by thermogravimetry

The mixtures used in the planned experiments are composed of HDH (commercial calcium sulfate hemihydrate $CaSO_4.0,5H_2O$), carbon or silica, and calcium chloride is precursor reactants and or catalysts. The section next describes the mixtures of samples.

To record the variation in the weight of the chemical compounds reacted under the effect's gradual increase in temperature used the ATG thermogravimetric analysis. The ATG included an electronic balance (Cahn 1100), the reactor composed from a vertical fine tube furnace, a helium or nitrogen gas transport system with the possibility of bringing the reaction medium into direct contact with the air, and a data acquisition system consisting of a computer equipped with a monitor for visualization.

The experimenter can adjust some parameters, such as the duration of the heating and its maximum temperature, while the rate of temperature change can be deduced from the data initially set in the oven. In a very small porcelain crucible, the samples of solid mixtures are placing and then introducing into the atmosphere of the reactor in contact with air. The ATG system programmed for gradual heating, from ambient temperature to 1000°C with a speed of 20°C/min, and subsequently, the parameters initialized in the system fix the temperature range dissociation already predicted by the thermodynamic analysis.

Products obtained and its analysis by X-ray diffraction (XRD).

The product returned by the thermogravimetric platform examined a thermodynamic study a posteriori to predict any constituents present in the reactions. This task therefore followed by an analysis in the XRD diffractometry device. Then, the outcome of the diffraction of the sample scanned has coordinated between PDFile and CIDD in the Match software. Through the database, species grouped regenerate the rateof RIR indicators. The instrument used is SHIMADZU brand (LabX, XRD61000), operates at a rate scanning speed of 0.02°C/min and in the range of 2θ from 10° to 70°, (the type of CuKα radiation, the voltage is 40kV, the current is 30 mA and λ= 1.5406 Å). This characterization equipment belongs to the analysis platform of the faculty of science.

Pyrometallurgy scenario: Preparation of the composition for the XRD analysis

For reasons of a small quantity of the sample (a few milligrams) used that subjected to a very high temperature of 1000°C, during the thermogravimetric analysis. From the mother's preparation, another sample taken. Then heated

in the tube furnace approximately the same temperature collected by the TG analysis system. The sample placed in a porcelain nacelle (boat), and thenintroduced into the furnace. As for the operating program, the time and temperature parameters initially saved. From these parameters, it is possible to deduce the heating rate.

The startup behavior of the Nabertherm B180 oven uses automatic program. Consequently, the tube furnace is heated according to the program initialized immediately after the command (start). If on the contrary, the temperature of the oven was higher than the set temperature T_1 the program is delayed until at the internal temperature of the tube furnace cools down and stabilizes at a value of T_1 + 10 ° C. Therefore, t_1(cooling duration) is not taken into account, and the program starts instantly for a period of t_2(increasing temperature duartion). It is this time that is used in the pyrometallurgical process.

Thermodynamic analysis: Decomposition of HDH:-

In general, the basis of predictions of the spontaneity and direction of a reaction or chemical process in a system is the free enthalpy change ΔG. The variation of the state function of the enthalpy depends only on the system equilibrium state. However, some gases can be involved in reactions within the system, which their partial pressures identify them. These quantities are often an obstacle clearly and precisely determining the evolution of the free enthalpy.

In addition, the ΔG° represented the change of state, where its evaluation is doneunder normal conditions of pressure and temperature, knowing that the pressures of the input gases involved are taken at the atmosphere [36]. When ΔG° is negative, the reaction is spontaneous at any temperature. On the other hand, if ΔG° is positive, the chemical reaction is unfavorable and cannotnever to be spontaneous in the reaction conditions.

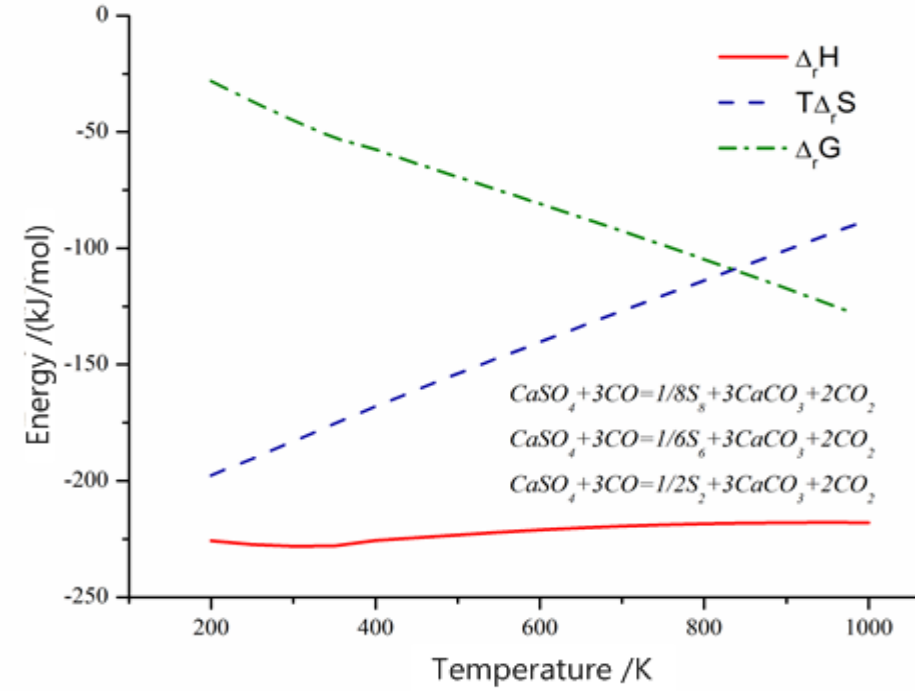
Examination on the compounds formed during the reduction of HDH.

What feature leads to the possibility of reduction reactions of CaSO4, which evolves to the generation of sulfur dioxide gas at a low temperature?Bear in mind that in the rich atmosphere of carbon monoxide, HDH is more reducible and more often spontaneously exothermic.However, in the thermodynamic analysis point of view, the most favorable reduction reactions of calcium sulfate generate the synthesis of calcium sulfide (CaS), lime (CaO) or calcite ($CaCO_3$). The production of these compounds is endothermic. Their enthalpy energies vary between 40 kJ/mol and 390 kJ/mol.

In addition, the reaction that occurs in a carbon monoxide atmosphere assumes the production immediate of elemental sulfur in a very probable, spontaneous, in which lime combines with carbon dioxide to synthesize calcite, leading to an exothermic reaction. Therefore, a release of a large amount of heat and the conversion of sulfur occurs depending on the temperature conditions found. The structure of sulfur changes gradually as the temperature increases and then evaporates into a gas phase at increasingly high temperatures.

In addition, under spontaneous conditions based on free enthalpy, the first gas only begins to appear at very high temperatures, far exceeding 1000°C. As for the triatomic gases, CSO and CS_2 can appear spontaneously at lowered temperatures. Researchers citing experimental studies from [36-37] show that when in the atmosphere of carbon monoxide, the calcium sulfate reduction generates carbon dioxide and releases the (SO_2).

Figure 3:- Variation of energies (Enthalpy, free enthalpy, and heat T.ΔS) for the reactions of production of elemental sulfur during the reduction of $CaSO_4$.



The atmosphere of carbon dioxide makes (SO_2) gas unstable and this gas will react with the gas all in the environment. The two gases (CO and SO_2) combine to produce carbonyl sulfide gas CSO. Another study confirmed that there are marginal amounts of CS_2 and S_2 gas [37-38].

The thermodynamic study that explicitly considers the most probable reactions, from the point of view of their free enthalpy analysis, makes it possible to show that the formation of calcite is parallel to the evolution of sulfur gas or vapor. Mainly from the (S_n) component varieties, the most stable form one is (S_8). In addition, both carbonyl sulfide (CSO) and carbon disulfide (CS_2) is close to the equilibrium point at elevated temperatures.Another tendency for the demonstrated reactions liberate the sulfur gases mentioned above, but in the presence of lime, they occur as spontaneous and favorable reactions at relatively high temperatures. The temperature is only suitable for reaction releasing sulfur dioxide (SO_2), and it is an appropriate reaction releasing (S_2), (CSO), (CS_2) and forming lime.

Conversion of gases containing sulfur to calcium sulfide.

After this substantial step, the gaseous sulfur species can react in a calcareous medium and promote the synthesis of calcium sulfide in exothermic reactions with enthalpic energy of between 133 kJ/mol and 1069 kJ/mol. In addition, the other exothermic can synthesize ($CaSO_3$) or (CAS), but with the participation of (SO_2(g)) with a heat input ~1000kJ/mol. Indeed, studies also show that the association of lime CaO carries out the reactions of conversion of sulfur compounds in the gaseous state [39]. All of these compounds are absorbed spontaneously and synthesize calcium sulfide (CaS). Therefore, the product end of the HDH reduction reactor can only be calcium sulfide (CaS).

Conversion of calcium sulfide (CaS) to elemental sulfur (S_8).

Calcium sulfide is a sulfur-containing compound. It can also serve as a medium for long-term storage of heat on the one hand and the sulfur product on the other. The fact that calcium sulfide is the most important of these syntheses achieves. Two successive steps lead to elemental sulfur in a reaction medium at room temperature. Both reactions are exothermic and spontaneous at lowers temperatures. At this stage of the process that generates heat is more than what the reduction of calcium sulfate needs, and that conforms to the following reactions:

$$CaS_{(s)} + CO_{2(g)} + H_2O_{(l)} \rightarrow H_2S_{(g)} + CaCO_{3(s)} \qquad \Delta_r H^{\circ}_{298} = -74.68\, kJ\,/\,mol \qquad \text{(Eq.3)}$$

$$H_2S_{(g)} + H_2SO_{4(aq)} \rightarrow \frac{1}{8}S_{8(s)} + \frac{4}{3}H_2O_{(l)} \qquad \Delta_r H^{\circ}_{298} = -89,28\, kJ\,/\,mol \qquad \text{(Eq.4)}$$

H_2SO_4 is a compound that is already available during the electrolytic process. The combustion of S generates SO_2, which is the principal input in electrolysis.

Carbon-adjuvanted HDH pyrometallurgical process:

At first glance, the pyrometallurgical process requires a temperature rise of at least 823K. Now, in the power unit ensuring the heat transport, this temperature found at the beginning of the decomposition of ethane as a thermally efficient coolant fluid for low temperatures. For performance reasons, the Brayton power unit authorize high temperatures [40], in which the fluid sCO_2 circulates in its 2 circuits, principal in and secondary[31]. The heat transfer fluid then transports heat through the secondary circuit to the reaction medium. Reduction of HDH in a carbon monoxide atmosphere is the most favorable reaction due to its spontaneity at lowers temperatures. The recovered thermal energy supposed from the cycle. We use it for the pyrolysis of carbon, which produces carbon monoxide. The carried out pyrolysis made in an ambient air atmosphere and catalyzed by adding calcium chloride $CaCl_2$, so the oxidation of carbon compond to carbon monoxide CO at a lower temperature than usual. Well, in an inert atmosphere, the figures Fig.4 and Fig.5 present the two possibilities, which favor thermodynamics, the formation of calcium sulfide with the release of carbon dioxide. With an energy requirement of over 500 kJ/mol, the former emits carbon monoxide and starts at a temperature of 730°C. While the second consumes 150 kJ/mol, and the emission of carbon dioxide begins at a temperature of 475°C. Once the carbon monoxide is in the atmosphere of the reaction medium, it will interact with the calcium sulfate, as shown in figures Fig.6 and Fig.7, the former contains only carbon monoxide gas, while the other adds interaction with carbon already present in the reaction medium. This result shows spontaneous exothermic reactions with more heat release when reacting with carbon monoxide alone, making it the most favorable [39]. The thermodynamic analysis of the reactions with the carried out carbon in the mixture for the four cases possible. Taking into account the intermediate reaction with carbon and carbon monoxide, we summarize the following:

1. The decomposition of calcium sulfate is directly favorable when carbon monoxide begins to release from a temperature of 725K and a calorific input> 500 kJ/mol.
2. Decomposition is favorable at a temperature of 450K with the release of carbon dioxide and a calorific input of approximately 175kJ / mol.
3. The spontaneous interaction of carbon monoxide and carbon causes HDH to decompose, resulting in elemental sulfur and calcite. Indeed, the formation of calcite released lot of heat.
4. Carbon monoxide is simply a gas atmosphere, spontaneously reduces calcium sulfate and releases carbon dioxide with little heat input.

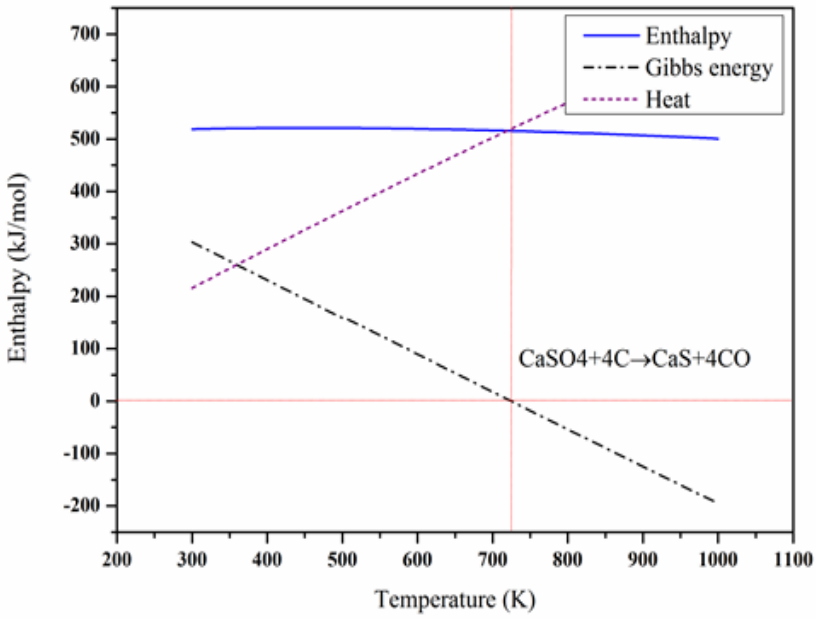


Figure 4:- Curves related to the thermodynamic study of the reaction of calcium sulfate and carbon with the generation of carbon monoxide.

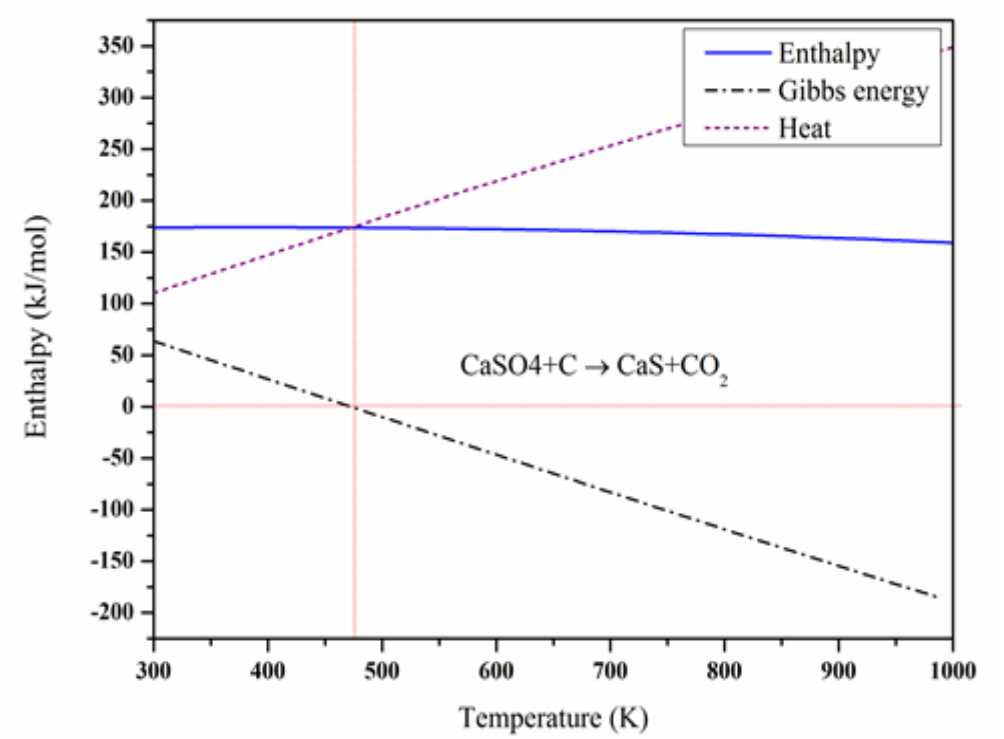


Figure 5:- Curves related to the thermodynamic study of the reaction of calcium sulfate and carbon with the generation of carbon dioxide.

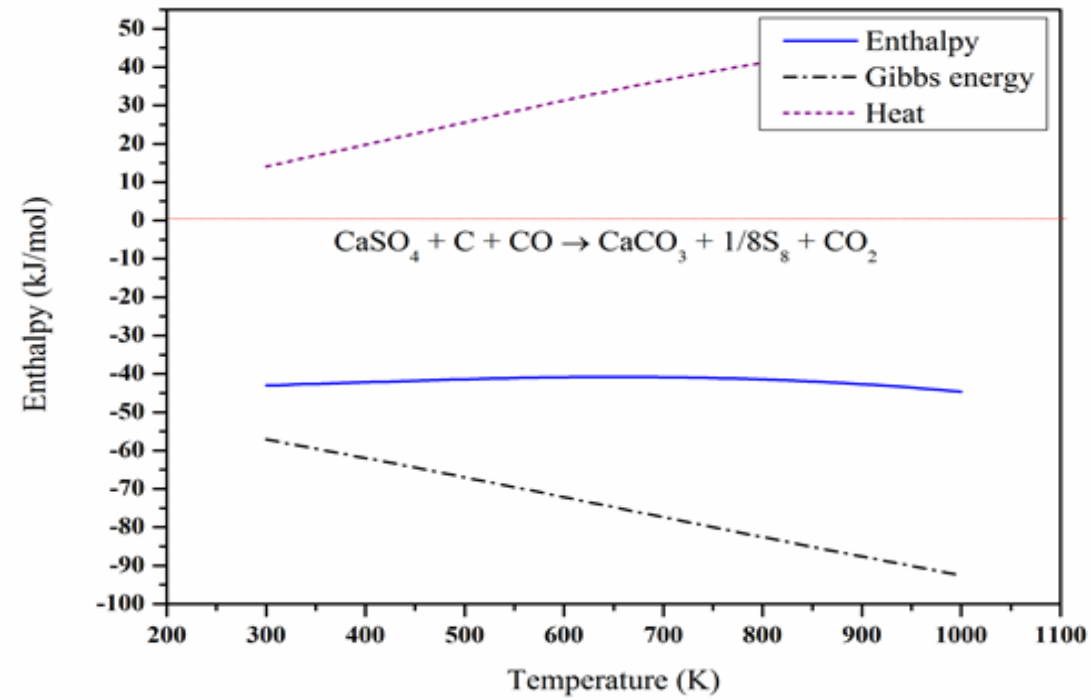


Figure 6:- Curves related to the thermodynamic study of the reaction of calcium sulfate and carbon in a carbon monoxide atmosphere.

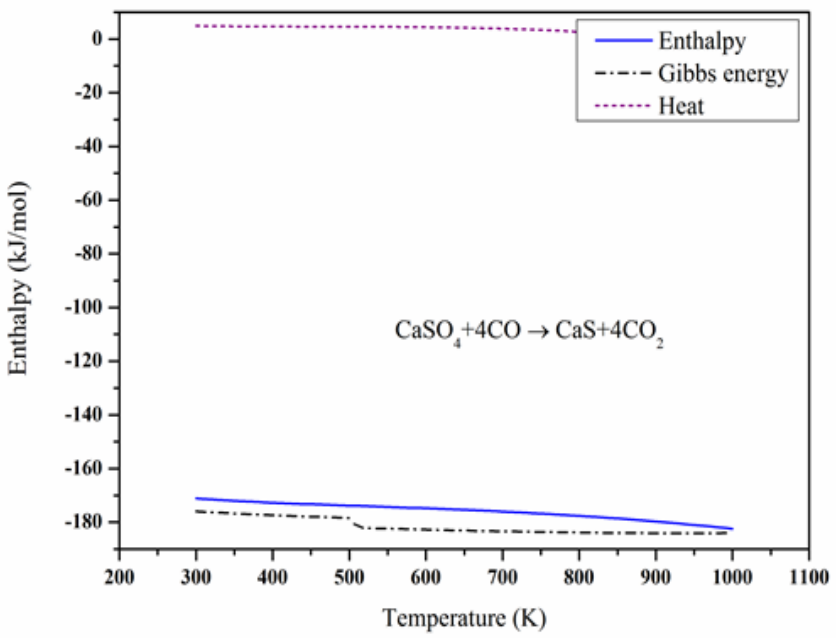


Figure 7:-curves related to the thermodynamic study of the reaction of calcium sulfate in a carbon monoxide atmosphere.

Experimental pyrometallurgical procedures in the presence of adjuvants:-

Before presenting the results and discussing them, it seemed reasonable to us to set out some experimental pyrometallurgical processes in the presence of adjuvants. In this case, of the figures Fig.8, Fig.9, and Fig.10 present the results of experimental work relating to the decomposition of calcium sulfate in an inert atmosphere with the addition of additives based on metal oxides, such as Al_2O_3, Fe_2O_3, and SiO_2 in addition to carbon[21], [41-42]. All these works show that the decomposition of calcium sulfate occurs at very high temperatures up to 1000°C, considered very high for operation from renewable energy sources; they obtained in the experiments cited in the literature [15-17].

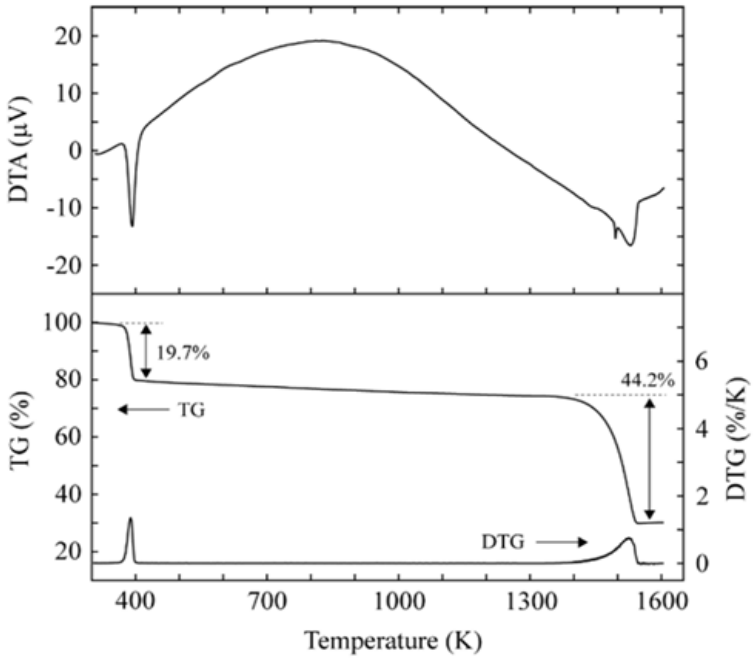


Figure 8:-TG/DTG/DTA thermograms of CaSO4.$_2H_2O$ with a heating rate of 10°C/min in a dry N_2 inert atmosphere.

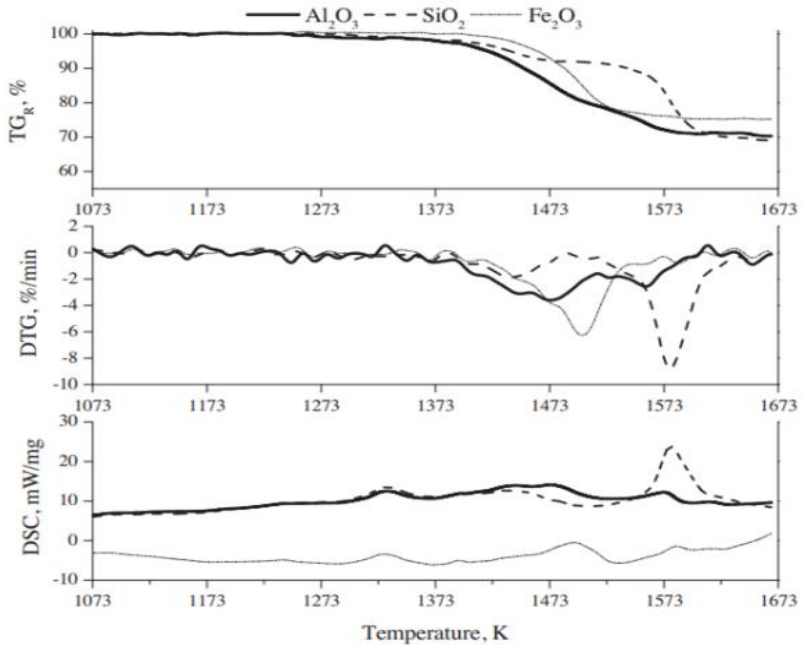


Figure 9:- TG/DTG/DSC curves during $CaSO_4$ doping with the adjuvant compounds Al_2O_3, Fe_2O_3, and SiO_2.

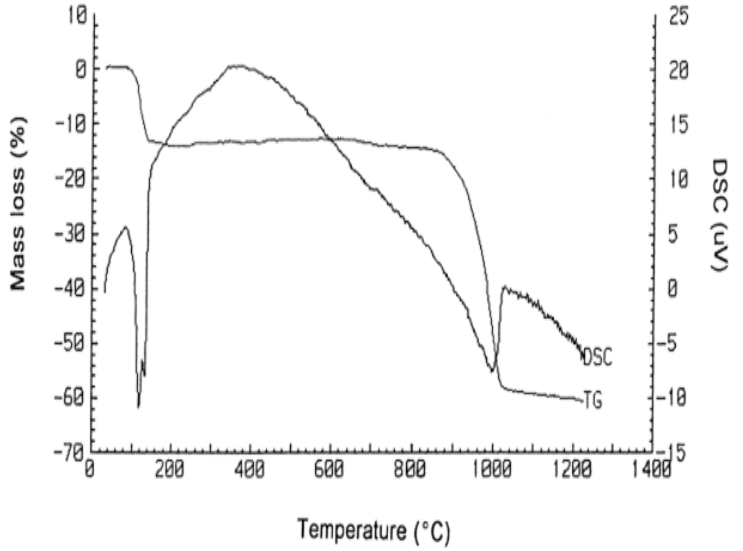


Figure 10:-TG and DSC curves when a stoichiometric mixture of C and $CaSO_4.2H_2O$ in an inert atmosphere and a heating rate of 5°C/min.

Results And Discussions:-

The thermogravimetric analysis focused on the reduction of calcium sulfate. Three combinations of reactions catalyzed by $CaCl_2$ with or without carbon in the mixture stand out:i) $CaCl_2$ adjuvant without reducing element, ii) Adjuvant $CaCl_2$ and the carbon-free oxidant SiO_2, iii) Adjuvant $CaCl_2$ and reducing carbon C(s). The auxiliaries compounds added are silicon dioxide SiO_2. It is an oxidant with an oxidation degree from 0 to + 4, carbon C(s) is a reducing element, and calcium chloride $CaCl_2$ is a catalyst that reduces the activation energy by kinetic effect. The mixtures of calcium sulfate and the aforementioned auxiliary substances produced in the stoichiometric ratio of three samples of: (HDH + $CaCl_2$, HDH + $CaCl_2$ + SiO_2 andHDH + $CaCl_2$ + C). Accordingly, the following TG thermogravimetric analyses were performed on each of these cases as shown in Figs.11, 12 and 13.

After heating the mixtures to 1000°C, the TG platform dataloger records weight measurements of each mixture immediately, and then displays mass losses in percentage mode and difference mode above. All curves at 174°C

have a loss rate of 10% at the first temperature drop. The last temperature is a state at which water evaporates out of HDH: $CaSO_4.0.5H_2O$. In particular, HDH converts into anhydrous sulfate $CaSO_4$. Furthermore, the dried carbon and calcium chloride leave traces of water in the mixture due to the condensation of water molecules on their surfaces. The $CaCl_2$ builder alone did not have much impact in the reaction medium, since the mixture did not lose considerable mass, almost plateauing between ~174°C and 1000°C. For temperatures below 1000°C, calcium chloride is inert for the reduction of calcium sulfate. In the second mixture of calcium sulfate, calcium chloride, and silica, weight loss is slow with increasing temperature up to about 700°C, at which point it accelerated to the maximum temperature of the TG program. According to previous research abovementionned, Fe_2O_3, Al_2O_3, and SiO_2 do not have an effect on decomposition of calcium sulfate until temperatures exceed 1000°C.

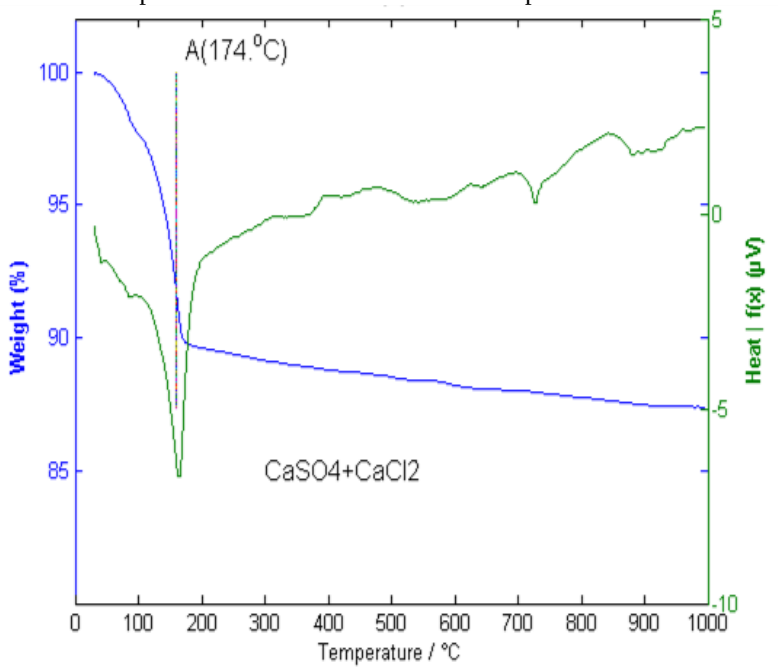


Figure 11:- An analysis of the weight loss TG of the sample containing HDH and calcium chloride.

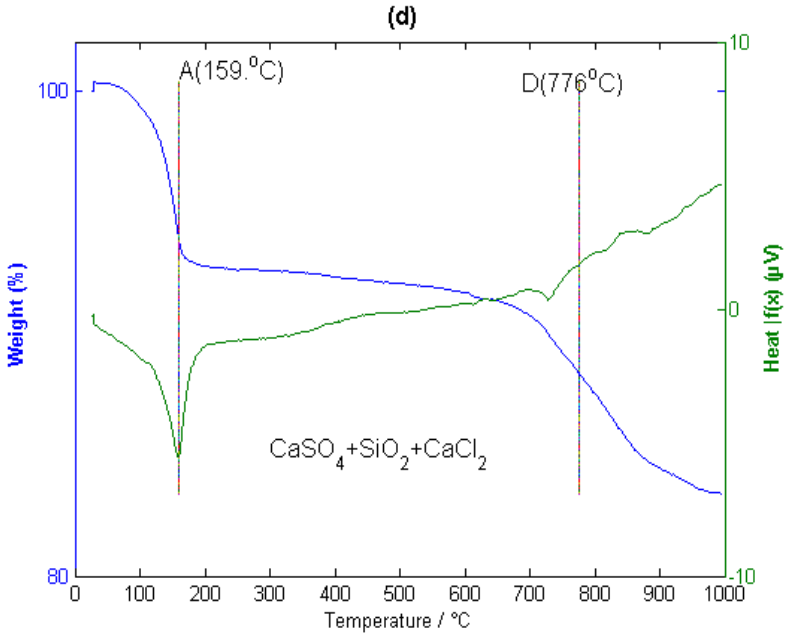


Figure 12:- An analysis of the weight loss thermogravimetrically conducted on the sample containing HDH, calcium chloride, and silicon dioxide.

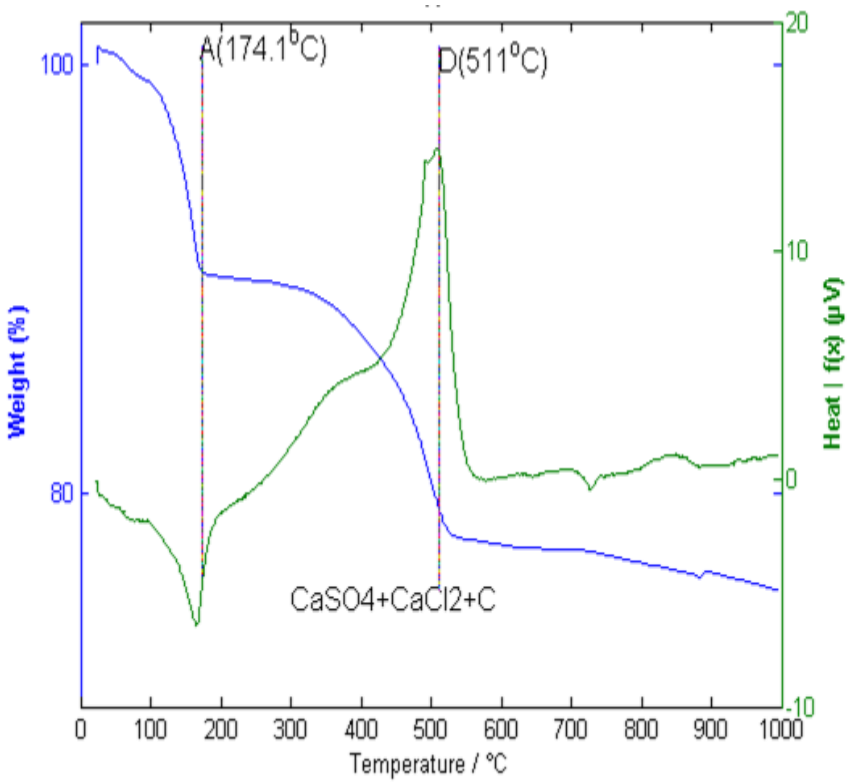


Figure 13:- Calcium chloride, and silicon dioxide.Calcium chloride and carbon weight loss thermogravimetric analysis.

Thermogravimetric analysis on the sample containing silicon dioxide SiO_2 shown in figure Fig.12, demonstarteno weight loss observed until temperatures reached 650°C. Calcium chloride $CaCl_2$ decomposes at a temperature of 350°C less when added to the mixture. When the sample contains a proportion of carbon plus $CaCl_2$, the highlightedmass losses in figure Fig.13 increase, and become more significant at temperatures of 300°C. Carbon monoxide and/or carbon dioxide are produced during the pyrolysis of carbon. Calcium sulfate directly consumes the gas from CO during its production. Sulfur compounds are created by reducing HDH. Due to exothermic reactions of the order of 540°C. This result is in complete agreement with the thermodynamic studies previously observed. On the other hand, there is another phase in this previous figure, which represents the percentage of 12.33%, which is the significant weight loss. It gradually appears in the temperature range of 180-600°C, confirming changes in the composition of the mixture, suggesting the existence of reactions that cause weight loss due to the generation of gas, and this rate of weight loss remains modest. In addition, the thermodynamic analysis previously carried out allows the synthesis of certain solid compounds. Specifically, the gradual weight loss of the sample clearly shows that the start temperature was recorded at about 300°C and ended at a temperature of 540°C. The conversion of this carbon mixture in question was exothermic, and the enthalpy of the transition phase reached 15 µV at a temperature of 515°C. The mass initially used was 18.1 mg, and the reduction temperature was around 480°C.

However, the decomposition temperature of calcium sulfate estimated by TG is currently recognized. A tube furnace roasts another sample taken from the parent composition and heated up to a value above this TG temperature decomposition. Moreover, when it comes out of the oven, XRD analysis identify the détails of composition.The quantity extracted from the TG platform is not sufficient for diffraction analysis. Therefore, in reality, the sample is taken from the parent batch ($CaSO_4$+$CaCl_2$+C) originally used in TG. This new sample is mounted on a porcelain basket, inserted in the heart of the oven, heated to a temperature of 600°C under air for 120 minutes, programmed at a heating rate of 20°/min, and for the same period analysis. It remains in the TG. The same observation made for the mixture ($CaSO_4$ + $CaCl_2$ + SiO_2).Illustration Figs.14 and 15 shows the results of the XRD of test samples.

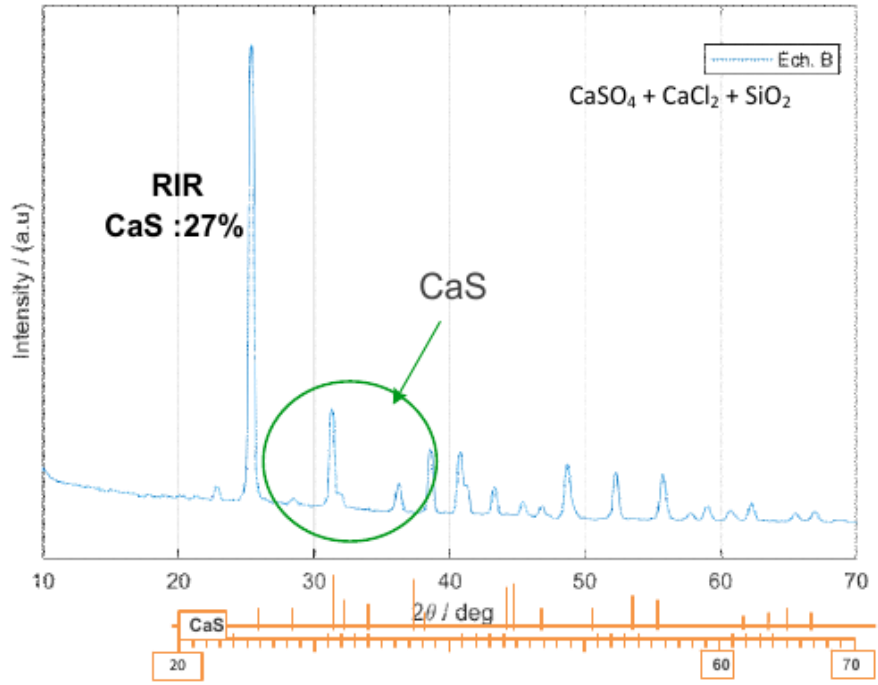


Figure 14:- XRD diagram of the powder restored from the thermal reactor in the presence of $CaCl_2$ and SiO_2.

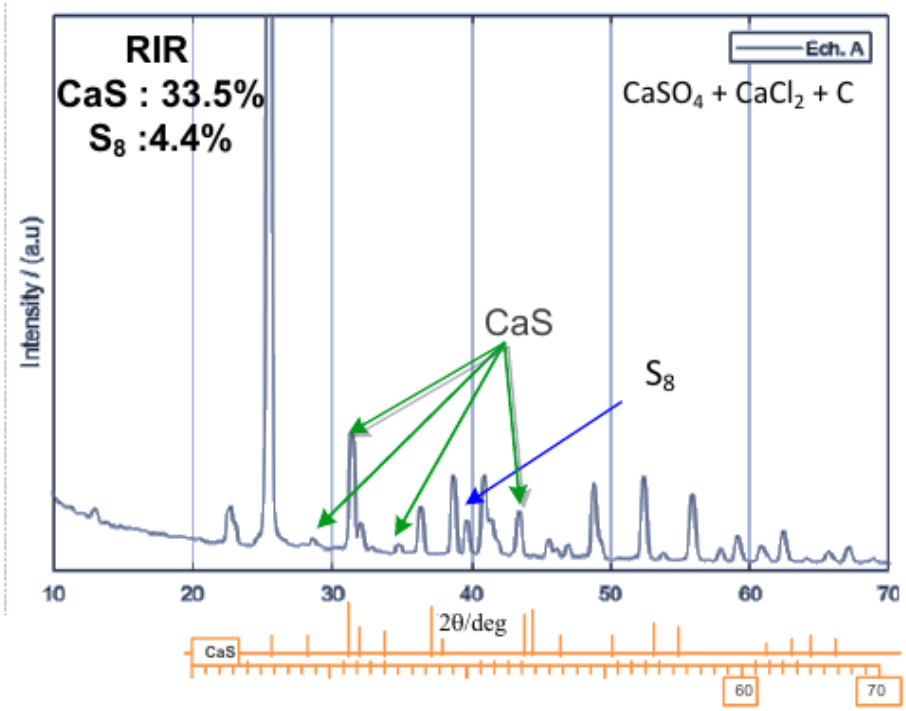


Figure 15:- XRD diagram of the powder generated in the reaction medium in the presence of CaCl2 and C.

The XRD diffraction map of the mixture ($CaSO_4$+$CaCl_2$+C) shows the valuable RIR rates: elemental sulfur S_8, calcium sulfide CaS, and the residual and reconstituted calcium sulfate of respectively, 4.4%, 33.5%, and 61%. This process is the pyrolysis of carbon to produce carbon monoxide, which reacts spontaneously at temperatures below 500°C. For dissociated $CaSO_4$ constituents which can only melt at temperatures above 1400°C, their melting temperature is relatively far in the program of laboratory furnaces and at a maximum temperature of 1000°C. The decomposition of $CaSO_4$ below 500°C to

produce S_8, CaS and CaO are amazing, but $CaCO_3$ is only a combination of the spontaneous exotherm of CaO limestone and CO_2. Therefore, the most likely way to form elemental sulfur, the research target, and the component of cyclo-octa-sulfur S_8, is a more stable form than other species. Sulfur alone has a melting point of about 120°C and a boiling point of about 450°C, from which it transformes into gas $S_6$and S_2 and volatilizes, giving a proportion of 4.4 %. In parallel, the XRD diffraction map of the mixture ($CaSO_4$ + $CaCl_2$ + SiO_2) shows the presence of the 27% calcium sulfide compound in terms of RIR rate.

The $CaCl_2$ adjuvant process discussed in this study is not the only mechanism that evolves the sulfur retention of HDH compounds. Instead, we suggest other adjuvants such as zinc sulfate. This adjuvant can help improve the dissociation process of calcium sulfate, which is the prospect of this work. However, the intermediates produced which cause chemical changes can catalyze the adjuvant. The last may explain the observation that the adjuvant $CaCl_2$ reduces the activation energy of carbon pyrolysis more efficiently and helps in reducing the temperature of decomposition of calcium sulfate in the current process. From a thermodynamic point of view, temperatures less to 487°C can also produce gas CS_2. This gas is flammable and quickly converts to carbon dioxide and sulfur dioxide in the presence of oxygen.

Conclusion:-

The reduction of the decomposition temperature of HDH is feasible in a reaction medium containing calcium chloride and some precursors. Feasibility and products predictions made by thermodynamic studies, analyzed by the thermogravimetric technique, and verified by X-ray diffraction.

The results show that HDH can react with carbon or silica precursors in attending catalysts such as calcium chloride. This component accelerates reducing the activation energy of its reaction using concentrating solar energy technology over a technically affordable temperature range.The observations made during this study show that some reactions occur with a mixture of carbon and HDH, with the adjuvant $CaCl_2$ promoting the oxidation of carbon. Subsequently emits carbon monoxide from the temperature of 480°C. This situation causes the natural and spontaneous decomposition of calcium sulfate. Consequently, by the pyrometallurgical process, the XRD analysis results in the outcomes with an RIR rate of CaS of about 33% (27% with silica), and the formation contains a modest quantity of elemental sulfur S_8/S_6 valued at about 4.4%. Therefore, the two components, (CaS) and (S_8) succeeding from the treatment of mixtures of HDH with carbon or silica show react at temperatures achievable with renewable energies, which evaluated from respectively 500°C and 750°C. At the same time, the presence of oxygen in the air prevents the formation of the toxic gas CS_2. On the other hand, avoiding the process of emitting carbon dioxide leads to its recovery in the mixer using water. Therefore, this task will convert CaO to $CaCO_3$ and produce H_2S. Sulfuric acid and hydrogen are usual products of Westinghouse electrolysis. When 1/3 of the sulfuric acid, produced helps generate H_2S, and finally, the elemental sulfur will yield spontaneously.

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