



Regeneration of a nickel carbonate desulfurization catalyst
by Glenn A Whan

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering
Montana State University
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Abstract:

The purpose of this investigation was to find the optimum conditions for regenerating, easily and economically, a spent nickel desulfurization catalyst. Two main steps in the regeneration are the oxidation of nickel sulfide to form nickel sulfate and wet chemical regeneration, i. e. precipitation of nickel carbonate using sodium carbonate. The nickel carbonate is then dried and used as an active desulfurization catalyst.

The oxidation step was investigated in a fluid oxidation unit to determine optimum conditions for producing a soluble sulfate in the hope of eliminating the use of excessive amounts of sulfuric acid, A sulfuric acid leach is used to sulfate all nickel not sulfated by oxidation. Optimum conditions for oxidation were found to be a temperature of about 850°F and a contact time of one to two hours.

Aside from initial activity, the value of a nickel catalyst is determined by the extent of catalyst utilization. Catalyst utilization, based on the percent of nickel converted to nickel sulfide, was investigated by testing variously prepared catalysts in a comparison unit. The comparison unit was designed so that various catalysts could be run under identical hydrofining conditions. Not only conditions of hydrofining but also conditions of wet chemical regeneration of the catalyst affect the extent of catalyst utilization, A study was made of catalyst utilization with respect to precipitation and digestion conditions and the effect of entrained salt, A catalyst demonstrating maximum sulfiding was precipitated when a slight excess of sodium carbonate was rapidly added to a solution of nickel sulfate, with little or no time allowed for digestion. Slight traces of entrained salt appeared to be beneficial to maximum catalyst utilization.

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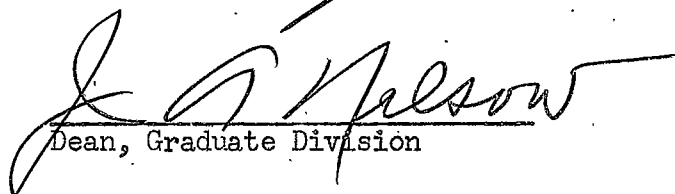
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TABLE OF CONTENTS

	page
ABSTRACT.	3
INTRODUCTION.	4
OXIDATION	7
Apparatus and Equipment.	8
Procedure.	9
Thermodynamic Calculations	10
Results.	13
WET CHEMICAL REGENERATION	15
Effect of Catalyst Utilization	16
Apparatus and Equipment.	18
Materials and Procedure.	20
Calculations	22
Results.	24
SUMMARY	28
ACKNOWLEDGEMENT	29
LITERATURE CITED.	30
APPENDIX.	31

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ABSTRACT

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INTRODUCTION

The ever-increasing demand for petroleum products and the depletion of high quality, low sulfur crudes has forced refiners to run more and more low quality, high sulfur crudes, such as those found in the Rocky Mountain area, West Texas, and California. Relative volumes of high sulfur crude oil produced in the United States have increased considerably over the last several years (9).

Increased use of high sulfur crudes has created a serious problem of desulfurization. High sulfur content in crude stocks results in products that demonstrate an objectionable odor, corrosiveness, and poor color stability. Also, difficulties have arisen with respect to sludge formation upon storage of fuel oils derived from high-sulfur crudes (11).

A considerable number of methods are already in existence for removing or changing the form of sulfur compounds present in petroleum distillates. These, however, are used for relatively low concentrations of sulfur compounds present in the more reactive form. High-sulfur contents in petroleum stocks are usually due to the presence of thiophenes and thiophanes that can be removed only by catalytic decomposition in the presence of hydrogen (2).

Nickel compounds or free nickel is an active catalyst for the desulfurization of hydrocarbon distillates in a hydrogen atmosphere (6) (7). The nickel or nickel compounds may be catalysts acting to remove the sulfur as hydrogen sulfide or may be reagents resulting in the formation of nickel sulfide. Nickel oxide supported on alumina or a similar support has been

used as a contact agent for removing sulfur compounds from light petroleum hydrocarbons without affecting the olefin content (8). Fischbach (4) has investigated the preparation of a nickel oxide desulfurization catalyst that can be used to remove even the most refractory sulfur compounds from fuel oil with little or no hydrogen consumption, producing a product of improved appearance, better odor, and greater stability.

However, aside from initial activity, the value of any catalyst is determined by two factors: the ease with which the initial activity can be restored after it has declined during use and the number of times such regeneration can be accomplished before it is necessary to discard the catalyst.

The purpose of this investigation was to determine the optimum conditions for regenerating, easily and economically, a spent nickel carbonate desulfurization catalyst. The general procedure of regeneration is the oxidation of spent nickel catalyst, that is in the form of nickel sulfide, forming nickel sulfate, and then the precipitation of nickel carbonate from a solution of nickel sulfate and sodium carbonate. The nickel carbonate can then be calcined to nickel oxide. However, the desulfurization activity of nickel carbonate is reported as greater than that of the calcined oxide (4).

The conditions of precipitation of nickel carbonate not only affect its activity but also greatly influence the ease with which it can again be regenerated after use. For this reason, a study was made of the conditions of regeneration to determine the optimum conditions for preparing or regenerating a nickel carbonate catalyst that can again be regenerated, easily and economically, after its activity has declined during use.

It has been stated that nickel or nickel compounds may desulfurize as a true catalyst in the presence of hydrogen, or as a chemical reagent with the formation of nickel sulfide. However, the nickel compounds used in this investigation will be referred to as catalysts, with the implication that they may or may not change chemically while desulfurizing.

OXIDATION

The first step in the regeneration of a spent nickel carbonate catalyst is the oxidation of nickel sulfide, forming nickel sulfate, with an oxygen containing gas. The economics of the regeneration is based to some extent on the oxidation step. Variables influencing oxidation are evaluated on the basis of the percent of total sulfur converted to a soluble sulfate. The remaining sulfur would be in the form of a sulfide and a basic sulfate. Nickel that is not in the form of either a sulfate or a sulfide would be predominately an oxide. This includes all nickel which was not converted to a sulfide in the hydrofining operation and all nickel oxide obtained from the oxidation of the sulfide or from the decomposition of the sulfate. These nickel oxides are not active desulfurization agents and are the least desirable from an economic standpoint because sulfuric acid will be required to complete the sulfation. The basic sulfate is preferable to the oxide, but again sulfuric acid will be used, just to dissolve this sulfate. Thus, the oxidation step was investigated to determine the optimum conditions for producing a soluble sulfate. The variables investigated were contact time and temperature.

APPARATUS AND EQUIPMENT

A fluid oxidation unit was constructed to oxidize spent nickel carbonate catalyst. The unit was constructed from standard pipe nipples, reducing couplings, and bushings, as shown in Figure 4. The unit was about 40 inches long with a maximum diameter of 3 inches and a minimum diameter of 1 inch. A heating coil with resistance of 110 ohms and a maximum output of 440 watts at 220 volts was used on the upper part of the unit, and a 22 ohm, 110-volt, and 550-watt coil was used on the lower part of the unit.

An air preheater, consisting of a metal reactor, 24 inches long and 3 inches in diameter, filled with steel balls, was used. Two 550-watt heating coils and one 440-watt coil were used to heat the preheater.

Both the fluid unit and preheater were heavily insulated with magnesia insulation material. The heating coils were controlled by "Powerstat" auto-transformers, and iron-constantan thermocouples were used with a potentiometer to measure temperatures.

PROCEDURE

At the start of a run, the reactor and preheater were heated to just below the desired temperature. Then the air flow was turned on and adjusted to the desired rate. When the reactor and preheater had reached the operating temperature, the air flow was turned off and spent catalyst was charged in through the top of the reactor. Then the air flow was turned on again, and the temperature and the air flow rate were held constant for the duration of the run. When the run was completed, the air flow and Powerstats were shut off. After the fluid reactor had cooled, the bottom connection was loosened and the oxidized catalyst was removed. This catalyst was then analysed for total sulfur and soluble sulfate.

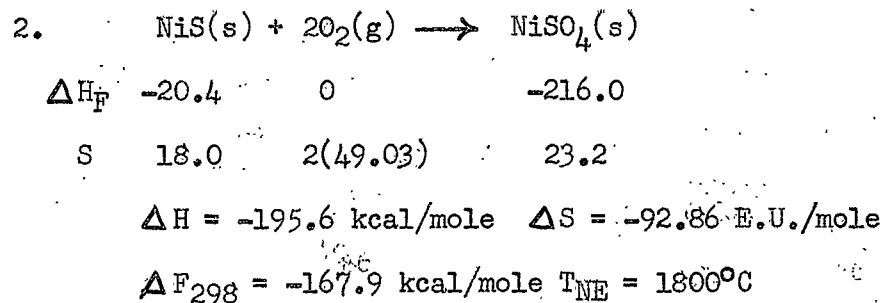
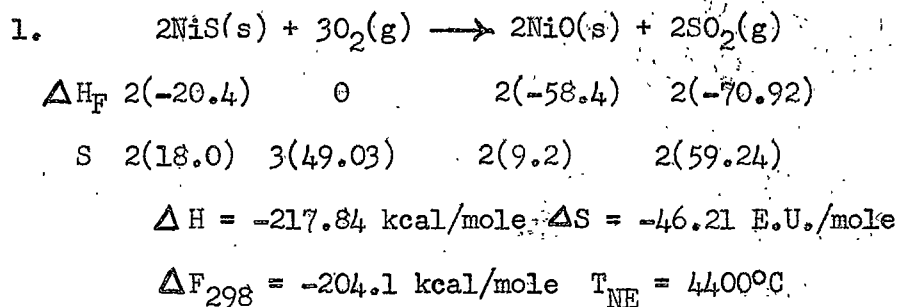
THERMODYNAMIC CALCULATIONS

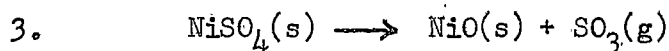
In order to help explain the mechanism of the oxidation of nickel sulfide, a thermodynamic investigation of the principal reactions was made. Also, two reactions involving steam and sulfur dioxide as the oxidizing agent were studied. The values for ΔS and ΔH at 298°K were used in the following equations:

$$\Delta F_{298} \approx \Delta H - T\Delta S$$

$$T_{NE} \approx \frac{\Delta H}{\Delta S}$$

The accuracy desired did not require calculations to compensate for variations in S and ΔH_F with temperature. ΔF_{298} stands for free energy at 298°K and T_{NE} stands for the temperature of neutral equilibrium.



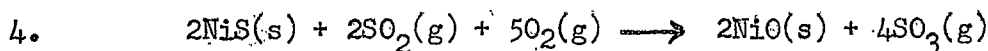


ΔH_F -216.0 -58.4 -104.2

S 23.2 9.2 63.8

$\Delta H = 53.4 \text{ kcal/mole}$ $\Delta S = 49.8 \text{ E.U./mole}$

$\Delta F_{298} = 38.7 \text{ kcal/mole}$ $T_{NE} = 800^\circ\text{C}$

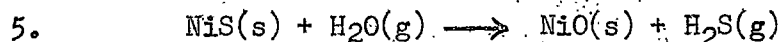


ΔH_F 2(-20.4) 2(-7092) 0 2(-58.4) 4(-104.2)

S 2(18.0) 2(59.24) 5(49.03) 2(9.2) 4(63.8)

$\Delta H = -351.06 \text{ kcal/mole}$ $\Delta S = -126.03 \text{ E.U./mole}$

$\Delta F_{298} = -313.5 \text{ kcal/mole}$ $T_{NE} = 2500^\circ\text{C}$



ΔH_F -20.4 -57.8 -58.4 -5.3

S 18.0 45.13 9.2 49.15

$\Delta H = 14.5 \text{ kcal/mole}$ $S = -4.78 \text{ E.U./mole}$

$\Delta F_{298} = 15.9 \text{ kcal/mole}$ $T_{NE} = -2750^\circ\text{C}$

Thermodynamically it is possible to produce nickel oxide from the oxidation of nickel sulfide. Unfortunately, the nickel oxide formed is not an active desulfurization agent. Also, the competing reaction, with the formation of nickel sulfate, has a strong tendency to go under the controlled oxidation conditions that must be used to protect the catalyst thermally.

It is shown (reaction 3) that nickel sulfate will decompose, forming sulfur trioxide, at about 800°C. Friedrich and Brickle (5) state that nickel sulfate will decompose into nickel oxide at 840°C, the decomposition

beginning at about 700°C. The oxide formed by this reaction is also not an active desulfurization catalyst.

From a thermodynamic standpoint, as shown in reaction 4, the presence of sulfur dioxide favors the oxidation of nickel sulfide. However, Milbauer and Tucek (10) state that nickel sulfide in the presence of sulfur dioxide yields nickel sulfate, but at the temperature where the sulfate tends to decompose.

The reaction involving the oxidation of nickel sulfide with steam is very unfavorable from a thermodynamic viewpoint. It has been found that the percent conversion is low at temperatures up to 1500°C. Even at 1500°C, it does not seem the reaction could ever become economically sound because of the cost of heating water to such a high temperature.

RESULTS

As stated before, the variables influencing the oxidation of nickel sulfide are evaluated on the basis of the percent of total sulfur converted to soluble sulfate. The results of the oxidation runs, along with the conditions used, are tabulated in Table I.

Effect of Temperature

Five runs were made to determine the optimum temperature for oxidation. The results of these runs have been plotted in Figure 1. The optimum temperature is shown to be about 850°F. However, the percent of total sulfur in the catalyst samples that had been run at 650°F was some three times that of the others. This tends to show that, while the higher temperatures may favor sulfation (reaction 2), they also tend to bring about the formation of the oxide (reaction 1) or the decomposition reaction or both. These latter reactions result in the formation of the undesirable nickel oxide. Unfortunately, in order to make the reaction rate of sulfation economically favorable, it is necessary to use as high a temperature as possible without causing excessive decomposition. The indications are that the optimum temperature is about 850°F.

Effect of Time

Runs 1-6 illustrate the effect of run time on the oxidation of nickel sulfide. The results of these runs have been plotted in Figure 2. Again, the catalyst sample run for one-half hour contained three times as much total sulfur as the others, indicating the tendency for the formation of the oxide to proceed at longer contact times. The decreasing percent of soluble sulfate in samples run for 4 hours and 8 hours indicates the decomposition of nickel

sulfate at such long contact times. The percent soluble sulfate formed is greatest between 1 and 2 hours, after which the decomposition reaction begins to predominate.

WET CHEMICAL REGENERATION

The second step in the regeneration of a spent nickel carbonate desulfurization catalyst is the wet chemical conversion of nickel sulfate to nickel carbonate. The nickel carbonate is then dried and used as an active desulfurization catalyst.

The first step in wet chemical regeneration is the leaching of spent catalyst with sulfuric acid. This step is necessary to sulfate all nickel that was not sulfided in the hydrofining unit and all nickel oxide obtained from the oxidation of the sulfide or from the decomposition of the sulfate. These nickel compounds react mole for mole with sulfuric acid, and as a consequence, large amounts of acid will be necessary if the percentage of nickel as nickel sulfate is low.

The second step is the precipitation of nickel carbonate. Here, the sulfated catalyst is put into solution and is mixed with a solution of sodium carbonate (calcium carbonate can also be used) forming a precipitate of nickel carbonate. The precipitate is then filtered and washed with water. Washing is a simple technical operation but has been found to be very important. Traces of sodium sulfate are not very detrimental to the initial activity of the catalyst, but appreciable amounts can not be tolerated (4). After the catalyst has been washed free of entrained salt, it is then dried and used as an active catalyst.

EFFECT OF CATALYST UTILIZATION

Desulfurization with a nickel catalyst is mainly dependent on two different competing reactions.



The first reaction results in the formation of nickel sulfide. When all available nickel is in the form of a sulfide, reaction 6 must end and reaction 7 will predominate. However, reaction 7 will proceed at a rate of uneconomic operation and the catalyst must be replaced.

The composition of spent catalyst at the beginning of regeneration is an important factor. Any unsulfided nickel remaining represents an economic loss, in that the catalyst was not used to its fullest extent, and that it increases the sulfuric acid consumption. As previously stated, all nickel that is not sulfided in the hydrofining unit must be leached with sulfuric acid.

Not only the conditions of hydrofining but also the method and conditions of regenerating the catalyst will affect the extent of catalyst utilization. Fischbach (4) has reported the factors that influence the precipitation of an active nickel desulfurization catalyst, but these are not necessarily the factors that will influence the precipitation of a catalyst that can be easily and economically regenerated. The activity of the catalyst is dependent upon both reactions 6 and 7, while the regeneration is dependent only upon the extent of reaction 6.

It would seem probable that any hydrofining conditions that would tend to repress reaction 7 would increase the ultimate percent of nickel sulfided. The conditions of precipitation that will produce a catalyst that will sulfide to the greatest extent are not evident from a thermodynamic standpoint and have been investigated. Conditions used for precipitation are shown in Table IV; solutions used for precipitation are described in Table III.

Another factor which affects catalyst utilization is purely physical. Very tightly pelleted catalyst without a porous support can contain active nickel compounds that cannot be physically reached to be utilized. Therefore, catalyst density must also be controlled by the conditions of precipitation.

APPARATUS AND EQUIPMENT.

A comparison unit was constructed to test variously prepared catalysts, to determine the conditions of hydrofining and the conditions of catalyst precipitation that will affect maximum catalyst sulfiding. A diagram of this unit is shown in Figure 5. The comparison unit, or comparator as it will be referred to, was designed so that various catalysts could be run under the same hydrofining conditions, giving a basis for comparing the results of sulfiding.

The comparator was made from a piece of 25 mm Pyrex glass tubing with a water-cooled condenser welded on to the bottom forming a solid unit about 36 inches long. The top of the tubing was fitted with the female portion of a 29/42 ground glass standard taper joint. A 35/25 ground glass ball joint was sealed to the bottom of the condenser.

Heat was supplied to the unit with a 550-watt heating coil controlled by a Powerstat. A thermowell, consisting of a piece of 6 mm Pyrex glass tubing sealed on one end, projected vertically into the catalyst bed. To measure temperatures, an iron-constantan thermocouple inserted in the thermowell was connected to a potentiometer. The entire unit was wound with asbestos tape and was covered with a thick layer of magnesia insulation.

The comparator unit was connected by means of the ball joint to a 1000 ml separatory funnel used as an effluent oil reservoir. Exhaust gas was passed through an ice condenser and a cadmium chloride precipitator to remove entrained liquids and hydrogen sulfide. A charge oil reservoir, consisting of a 500 ml separatory funnel, was connected to a bellows pump.

Oil was pumped continuously from the reservoir to the top of the comparator. Hydrogen was introduced into the comparator above the oil inlet. Hydrogen rate, regulated by a needle valve, was measured with a mercury manometer and orifice.

MATERIALS AND PROCEDURE

Charge oil used in this investigation was a straight-run, clear fuel oil. In addition, the oil used in runs 7 and 8 was sand treated. The sulfur content of these charge oils varied from 2.09 to 2.20 percent by weight. Inspection data for the charge oils are presented in Table II.

To prepare the comparator for a run, about 1.0 gram of pyrex glass wool, serving merely as a catalyst support, was placed in the comparator just below the thermowell. The catalyst to be tested for maximum sulfiding was weighed and mixed with one-eighth inch porcelain fish spines and was then charged to the comparator. The fish spines prevented the fine catalyst from caking and plugging the unit. A layer of one-quarter inch fish spines, serving as a preheat section for the oil, was placed on top of the catalyst bed. The charge oil reservoir was filled with oil that had been previously weighed. All ground glass joints were greased and clamped in place, and the unit was then ready for operation.

The Powerstat was turned on, and while the comparator was heating, a small amount of hydrogen was allowed to pass through the unit. When the desired temperature had been attained, the pump, calibrated to deliver approximately 420 grams of oil per hour, was turned on, and the hydrogen flow was adjusted to the desired rate. Oil samples were periodically withdrawn from the effluent oil reservoir, weighed, and analysed for sulfur content.

At the end of the desired run time, the pump and Powerstat were turned off, but hydrogen was allowed to flow through the unit for a few additional

minutes to remove all oil from the catalyst bed. After the unit had cooled somewhat, its entire contents were removed and weighed. The spent catalyst was then analysed for the percent of total nickel sulfide. Oil remaining in the effluent reservoir was removed and analysed.

Oil samples that were to be analysed were given a caustic wash to remove any hydrogen sulfide. Sulfur content of the oil was determined by the conventional lamp-sulfur method, as described in the A.S.T.M. Manual of Standards (1).

CALCULATIONS

After a catalyst sample had been run in the comparator, the amount of sulfur removed from the oil was calculated. The amount of nickel in the catalyst had been determined by analysis before it was run. From these two figures a value for the percent nickel as nickel sulfide was calculated, based on the stoichiometric relationship between nickel and sulfur in a monosulfide. This stoichiometric percent is, in all probability, not correct for the following two reasons: some of the sulfur was removed from the oil as hydrogen sulfide, and the sulfur that did form nickel sulfide could have been contained as a polysulfide.

In order to obtain a more accurate figure for percent nickel as nickel sulfide, each spent catalyst was analysed for total nickel and total sulfur. However, this figure was again based on a monosulfide.

Using both figures for percent nickel sulfided, the sulfiding abilities of variously precipitated catalysts were compared. Due to sulfur removed as hydrogen sulfide the stoichiometric percent should be greater than the analytical percent. From this correlation, the relative "true catalytic" activities of the various catalysts were observed. A catalyst that demonstrates a stoichiometric percent that is much higher than the analytical percent would indicate that much of the sulfur had been removed from the oil as hydrogen sulfide.

Calculations for the various runs are included in Table VI, along with the hydrofining conditions. Oil was withdrawn from the effluent reservoir every hour in the first 8 runs and every four hours in remaining runs.

The weight of oil passing through the unit during each time interval between samples was corrected to account for losses due to cracking which were divided as equally as possible among the time intervals. The weight of oil before correction is the total effluent oil, while the weight of oil after correction is the total oil charged. Space velocity, reported as grams of oil per gram of catalyst per hour, was based on the total charge oil.

The amount of sulfur removed during each time interval was determined by multiplying the weight of oil after correction by the difference between the percent sulfur in the charge oil and the percent sulfur in the effluent oil for that time interval. The percent nickel sulfided was calculated from the total grams of sulfur removed from the oil.

Many catalysts demonstrate an apparent nickel sulfided greater than 100 percent. However, due to sulfur removed as hydrogen sulfide and the method of calculation, it is possible to have an apparent percent greater than 100 percent.

RESULTS

As previously stated, the variables of precipitating a catalyst that could be converted almost entirely to nickel sulfide during hydrofining were investigated. Also, the conditions of hydrofining conducive to maximum sulfiding were investigated. The results of the comparator runs are tabulated in Table V.

Run Time

A sample was taken every hour in the first 8 runs to determine the time required to sulfide a catalyst to its greatest extent. As the run progressed, the sulfur content of the oil samples got steadily higher, until after 4 to 8 hours, the sulfur content of the effluent oil was as high as that of the charge oil. Since sulfur was no longer being removed from the oil, the catalyst was no longer being sulfided. In some runs, the sulfur content of the effluent oil did not get as high as that of the charge oil, due to sulfur removed as hydrogen sulfide. In Figure 3, time in hours is plotted against sulfur content of effluent oil. From these data, it was decided that a run time of eight hours was sufficient to sulfide any catalyst to completion.

Effect of Temperature

Four runs were made varying the temperature from 525°F to 725°F. The lowest temperature, 525°F, appeared to favor formation of nickel sulfide. Higher temperatures are more favorable for the removal of sulfur as hydrogen sulfide. However, at 725°F the results were very poor and appreciable cracking was noticeable.

Effect of Hydrogen Rate

The effect of hydrogen rate was studied in runs 3, 5 and 7. The lowest hydrogen rate proved to induce maximum sulfiding. This is probably due to the fact that a higher hydrogen rate favors the removal of sulfur as hydrogen sulfide. In fact, any hydrofining conditions that would favor removal of sulfur, as hydrogen sulfide would not be optimum for maximum catalyst sulfiding.

Method of Adding Solutions

Relationship between maximum sulfiding and the method of adding solutions is demonstrated in runs 10, 12, 13, and 14. For two of the runs, catalysts were precipitated by adding nickel sulfate solution to a sodium carbonate solution, and for the other two, catalysts were precipitated by adding carbonate to sulfate. Results show that maximum sulfiding is obtained when the catalyst is precipitated by adding carbonate to sulfate. Coykendall (3) reported that a nickel catalyst of highest activity is obtained when sodium carbonate is added to a sulfate solution.

Fischbach (4) reported a definite relationship between the method of adding solutions and the physical characteristics of the resultant catalyst. When the sulfate solution was added to a carbonate solution, the catalyst was very granular and could not be extruded into "noodles." When the carbonate was added to a sulfate, the catalyst appeared to be very finely divided and was readily extrudable. This physical characteristic could help to explain why the latter method also produces a catalyst that will exhibit maximum sulfiding.

Effect of Excess Carbonate

The effect of precipitating by using an excess of the stoichiometric quantity of sodium carbonate is demonstrated in runs 10, 11, and 12. The data indicate that maximum sulfiding can be obtained with a catalyst that has been prepared by precipitating with stoichiometric quantities of carbonate or just a slight excess. Ueno (12) reported that nickel hydrogenation catalysts have the greatest activity when a slight excess of sodium carbonate is used.

Precipitation and Digestion

Several runs were made to determine the effect of precipitation and digestion conditions on the extent of sulfiding. Sample P-31 was precipitated at 71°F - 73°F and was digested at the same temperature. Samples P-30 and P-37 were precipitated at 188°F - 192°F and 206°F - 209°F respectively and were digested at the same temperatures. Results of the comparator runs indicate that maximum sulfiding is obtained when the catalyst is precipitated at the lower temperatures. Sample P-37 was precipitated over a time interval of 72 minutes, while P-43 was precipitated over a time interval of 15 minutes. Sample P-37 was digested for 60 minutes and P-44 was not digested at all. Results show that precipitation over a short time interval, with very little or no digestion, results in a catalyst that will demonstrate maximum sulfiding. Thus, the optimum conditions of precipitation and digestion appear to be rapid precipitation at room temperature with little time allowed for digestion.

Fischbach (4) reports that greater activity is obtained from a nickel catalyst when precipitation is carried out at the boiling point with

appreciable time allowed for digestion. Also, nickel carbonate is insoluble in cold water. If precipitation and digestion are carried out at the boiling point, the amount of nickel lost in the filtrate will be minimized.

Effect of Entrained Salt

Runs 17, 18, and 22 illustrate the effect of entrained salt upon catalyst sulfiding. Samples P-39-A, P-45, and P-37 were water washed once with 100 ml., three times with 100 ml., and three times with 340 ml., respectively, following filtration. Sulfiding figures indicate that the more the catalyst is washed, the less it will sulfide. Thus, it could be concluded that the presence of traces of sodium sulfate, as an entrained salt, is beneficial to maximum sulfiding. However, an appreciable amount of entrained salt is extremely detrimental to catalyst activity (4).

SUMMARY

The results and conclusions of this investigation may be summarized as follows:

1. Optimum conditions for the oxidation of a spent nickel catalyst, based on the percent soluble sulfate produced, are a temperature of about 850°F and a contact time of one to two hours.
2. Hydrofining conditions conducive to maximum catalyst utilization are a relatively low temperature of 525°F and a relatively low hydrogen rate.
3. Maximum sulfiding is obtained from a catalyst precipitated by adding a slight excess of sodium carbonate solution to a nickel sulfate solution.
4. Rapid precipitation at room temperature, with little or no digestion, results in a catalyst that will demonstrate maximum sulfiding.
5. A large amount of entrained salt is extremely detrimental to catalyst activity, but traces tend to promote maximum catalyst utilization.

ACKNOWLEDGEMENT

The author wishes to acknowledge the courtesy of the Husky Oil Company, who furnished the fuel oil and prepared the catalyst samples used in this investigation. The Husky Oil Company also performed much of the chemical analysis that was needed.

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APPENDIX

	page
Table I	Oxidation Conditions and Results 32
Table II	Inspection Data for Charge Oil 33
Table III	Solutions Used in Catalyst Precipitation 34
Table IV	Conditions Used in Catalyst Precipitations 35
Table V	Comparator Run Results 36
Table VI	Comparator Run Conditions and Calculations 37
Figure 1	Effect of Temperature on Oxidation 44
Figure 2	Effect of Time on Oxidation 45
Figure 3	Effect of Run Time on Comparator Runs. 46
Figure 4	Fluid Oxidation Unit 47
Figure 5	Comparator Unit. 48

TABLE I
OXIDATION CONDITIONS AND RESULTS

Run No.	Time Hrs.	Temperature of	Percent Total Sulfur	Percent Sulfur as Soluble Sulfate
1	1/2	850	10.18	9.14
2	1	850	3.72	72.85
3	2	850	3.85	73.25
4	3	850	3.67	65.67
5	4	850	3.91	66.75
6	8	850	3.88	60.26
7	4	650	10.89	36.82
8	4	1150	3.85	48.83
9	2	644	9.40	35.90

TABLE II
INSPECTION DATA FOR CHARGE OIL

	<u>Regular</u>	<u>Sand Treated</u>
A.P.I. at 60°F	30.6	30.5
Sp. Gr.	0.8729	0.8735
Average Mol. Wt.	222	222
Bromine No.	7.57	9.24
Wt. % Sulfur	2.09-2.20	2.20
Wt. % Hydrogen	10.9	10.9
A.S.T.M. Distillation		
I.B.P.	425°F	385°F
5%	504	499
10	520	519
20	536	536
30	548	547
40	558	555
50	567	566
60	575	575
70	584	584
80	594	595
90	611	613
95	625	631
E. P.	652	651
Recovered	99.0 %	99.0 %
Residue	0.8 %	0.8 %
Loss	0.2 %	0.2 %

TABLE III
SOLUTIONS USED IN CATALYST PRECIPITATION

Nickel Sulfate Solutions

Solution	Ingredients		Specific Gravity
	Grams Commercial NiSO ₄	ml H ₂ O	
A	Leached from spent Catalyst with H ₂ SO ₄		1.2529 at 28.9°C
B	858	2994	1.1458 at 24.5°C
C	843	1950	1.2060 at 23.9°C
D	843	1950	- - -
E	843	1951	- - -

Sodium Carbonate Solutions

Solution	Grams Na ₂ CO ₃ per gram of solution
A	0.1860
B	0.2300
C	0.2301
D	0.2298

TABLE IV
CONDITIONS USED IN CATALYST PRECIPITATIONS

Cat.	Sol'n	NiSO ₄		Sol'n	Na ₂ CO ₃		Added To Sol'n	Precipitation Temp °F	Time Min.	Digestion Temp °F	Time Min.	Water Wash cc per Wash	Wash No. of Washes
		cc	Gms		cc	Gms							
P-25	A	125.0	21.23	A	70.0	15.59	Na ₂ CO ₃	Boil	70	Boil	60	340	3
P-26	A	125.0	21.26	A	80.0	17.82	Na ₂ CO ₃	Boil	80	Boil	60	340	3
P-27	A	125.0	21.26	A	140.0	31.18	Na ₂ CO ₃	(Boil 207-209)	80	Boil 206	60	340	3
P-28	A	125.0	21.26	A	72.5	16.15	NiSO ₄	Boil	72	Boil	60	340	3
P-29	A	125.0	21.26	A	145.0	32.29	NiSO ₄	(Boil 203-205)	80	Boil 205	60	340	3
P-30	A	125.0	21.26	A	72.5	16.15	Na ₂ CO ₃	188-192	72	187-193	60	340	3
P-31	A	125.0	21.26	A	72.5	16.15	Na ₂ CO ₃	71-73	72	74	60	340	3
P-37	B	136.3	19.56	A	72.5	16.15	Na ₂ CO ₃	(Boil 206-209)	72	Boil 207	60	340	3
P-39- A	B	136.3	19.56	A	72.5	16.15	NiSO ₄	(Boil 203-204)	72	Boil 205	60	100	1
P-42	B	136.3	19.94	A	72.5	16.15	Na ₂ CO ₃	76.5-79	72	Boil 205	60	340	3
P-43	B	136.3	19.56	A	72.5	16.15	Na ₂ CO ₃	(Boil 204-206)	15	Boil 205	65	340	3
P-44	B	136.3	19.56	A	72.5	16.15	Na ₂ CO ₃	(Boil 205-208)	72	- -	0	340	3
P-45	B	136.3	19.56	A	72.5	16.15	NiSO ₄	(Boil 204-206)	72	Boil 206	60	100	3
P-48	B	136.3	19.56	A	130.0	28.95	NiSO ₄	(Boil 202-207)	80	Boil 207	60	340	3
P-55- B	C	98.7	19.49	A	65.0	14.48	Simul- taneous	(Boil 200-205)	72	Boil 206	90	340	3
29-3	D	2673	444.4	B&C	1180	335.2	Na ₂ CO ₃	Boil	60	Boil	60	1000	2
29-4- 5	(E) (C)	2223 119.7	444.4 23.64	D	1160	329.3	NiSO ₄	Boil	60	Boil	60	1000	2

TABLE V
COMPARATOR RUN RESULTS

Run No.	Catalyst	Stoichiometric Percent Sulfided	Analytical Percent Sulfided
1.	NiCO ₃	46.6	- -
2.	NiCO ₃	34.7	- -
3.	NiCO ₃	47.9	- -
4.	NiCO ₃	45.2	60.2
5.	NiCO ₃	55.0	62.8
6.	NiCO ₃	59.0	67.2
7.	29-4	35.1	49.8
8.	29-5	26.0	42.2
9.	29-3	111	59.3
10.	P-25	120	54.8
11.	P-26	129	52.6
12.	P-27	-	44.2
13.	P-28	49.8	45.2
14.	P-29	82.6	42.8
15.	P-30	52.7	44.8
16.	P-31	65.2	47.2
17.	P-37	83.7	45.9
18.	P-39-A	115	62.4
19.	P-42	87.7	52.3
20.	P-43	110	61.7
21.	P-44	97.2	49.0
22.	P-45	140	54.5
23.	P-48	128	57.2
24.	P-55-B	116	60.5

TABLE VI
COMPARATOR RUN CONDITIONS AND CALCULATIONS

Run No.	Catalyst	Wt. gms.	Temp. OF	Space Velocity gms oil gm cat. hr.	H ₂ rate STP ft ³ /hr	Time Hrs.	Wt. Oil before correction gms.	Losses gms.	Wt. oil after correction gms.	Percent Sulfur	Sulfur removed gms	Nickel in Catalyst gms	Percent nickel sulfided
1	NiCO ₃	23.5	625	17.5	2.46	0	---	---	---	2.090	---	9.87	46.6
						1	394.3	6.7	401.0	1.682	1.636		
						2	405.4	6.7	412.1	1.948	0.585		
						3	406.7	6.7	413.4	2.020	0.289		
						4	402.6	6.7	409.3	2.090	0.000		
						5	414.8	6.7	421.5	2.090	0.000		
						6	421.7	6.7	428.4	2.090	0.000		
						7	424.0	6.8	430.8	2.090	0.000		
						8	<u>371.7</u>	6.8	<u>378.5</u>	2.090	<u>0.000</u>		
						3241.2		3295.0		2.510			
2	NiCO ₃	23.5	725	17.3	2.46	0	---	---	---	2.090	---	9.87	34.7
						1	372.6	5.6	378.2	1.737	1.335		
						2	399.4	5.6	405.0	1.990	0.405		
						3	403.7	5.6	409.3	2.060	0.123		
						4	411.1	5.6	416.7	2.090	0.000		
						5	413.6	5.7	419.3	2.090	0.000		
						6	393.3	5.7	399.0	2.090	0.000		
						7	<u>412.8</u>	5.7	<u>418.5</u>	2.090	<u>0.000</u>		
						2806.5		2846.0		1.863			
3	NiCO ₃	24.0	525	17.0	2.46	0	---	---	---	2.090	---	10.10	47.9
						1	356.1	5.7	361.8	1.702	1.404		
						2	410.2	5.7	415.9	1.905	0.769		
						3	406.3	5.8	412.1	1.998	0.379		
						4	417.8	6.8	423.6	2.070	0.085		

TABLE VI (continued)
 Comparator Run Conditions and Calculations

Run No.	Catalyst	Wt. gms.	Temp. °F	Space Velocity $\frac{\text{gms oil}}{\text{gm cat hr}}$	H ₂ rate STP ft ³ /hr	Time Hrs.	Wt oil before correction gms	Losses gms	wt oil after correction gms	Percent Sulfur	Sulfur removed gms	Nickel in Catalyst gms	Percent nickel sulfided
3	NiCO ₃	24.0	525	17.0	2.46	5	419.1	5.8	424.9	2.090	0.000	10.10	47.9
						6	402.6	5.8	408.4	2.090	0.000		
						7	407.5	5.8	413.3	2.090	0.000		
							<u>2819.6</u>		<u>2860.0</u>		<u>2.637</u>		
4	NiCO ₃	24.0	575	17.1	2.46	0	---	---	---	2.090	---	10.10	45.2
						1	390.3	4.9	395.2	1.748	1.352		
						2	305.1	4.9	410.0	1.970	0.492		
						3	409.2	4.9	414.1	2.010	0.331		
						4	403.6	4.9	408.5	2.035	0.225		
						5	418.4	5.0	423.4	2.070	0.085		
						6	410.8	5.0	415.8	2.090	0.000		
							<u>2437.4</u>		<u>2467.0</u>		<u>2.485</u>		
5	NiCO ₃	24.0	525	17.1	2.98	0	---	---	---	2.140	---	10.10	55.0
						1	371.8	5.2	377.0	1.668	1.780		
						2	408.6	5.2	413.8	1.998	0.588		
						3	409.2	5.2	414.4	2.050	0.373		
						4	423.0	5.2	428.2	2.100	0.171		
						5	405.9	5.3	411.2	2.120	0.082		
						6	399.5	5.3	404.8	2.130	0.040		
						7	411.3	5.3	416.6	2.140	0.000		
							<u>2829.3</u>		<u>2866.0</u>		<u>3.034</u>		

TABLE VI (continued)
 COMPARATOR RUN CONDITIONS AND CALCULATIONS

Run No.	Catalyst	Wt. gms.	Temp. OF	Space Velocity gms oil gm cat hr	H ₂ rate STP ft ³ /hr	Time Hrs.	Wt. oil before correction gms.	Losses gms.	Wt. oil after correction gms.	Percent Sulfur	Sulfur removed gms	Nickel in Catalyst gms	Percent nickel sulfided
6	NiCO ₃	24.0	525	17.1	1.89	0	---	---	---	2.140	---	10.10	59.0
						1	411.1	1.3	412.4	1.732	1.682		
						2	400.3	1.3	401.6	1.972	0.675		
						3	407.1	1.4	408.5	2.055	0.347		
						4	422.7	1.4	424.1	2.070	0.297		
						5	402.0	1.4	403.4	2.110	0.121		
						6	410.8	1.4	412.2	2.110	0.124		
						7	416.4	1.4	417.8	2.140	0.000		
							<u>2870.4</u>	<u>2880.0</u>			<u>3.246</u>		
7	29-4	6.5	525	64.3	1.89	0	---	---	---	2.200	---	3.29	35.1
						1	402.8	4.4	407.2	2.120	0.326		
						2	389.5	4.4	393.9	2.160	0.158		
						3	407.1	4.4	411.5	2.165	0.144		
						4	421.0	4.4	425.4	2.200	0.000		
						5	414.2	4.4	418.6	2.200	0.000		
						6	424.8	4.4	429.2	2.200	0.000		
						7	423.0	4.5	427.5	2.200	0.000		
						8	430.2	4.5	434.7	2.200	0.000		
							<u>3312.6</u>	<u>3348.0</u>		<u>0.628</u>			
8	29-5	8.1	525	51.9	1.89	0	---	---	---	2.200	---	4.10	26.0
						1	417.1	2.4	419.5	2.140	0.251		
						2	398.7	2.5	401.2	2.160	0.161		
						3	418.0	2.5	420.5	2.170	0.126		
						4	424.3	2.5	426.8	2.190	0.043		
						5	411.3	2.5	413.8	2.200	0.000		

TABLE VI (continued)
 COMPARATOR RUN CONDITIONS AND CALCULATIONS

Run No.	Catalyst	Wt. gms.	Temp. OF	Space Velocity $\frac{\text{gms oil}}{\text{gm cat hr}}$	H ₂ rate STP ft ³ /hr	Time hrs.	Wt oil before correction gms	Losses gms	Wt oil after correction gms	Percent Sulfur	Sulfur removed gms	Nickel in Catalyst gms	Percent nickel sulfided
8	29-5	8.1	525	51.9	1.89	6	425.1	2.5	427.6	2.200	0.000	4.10	26.0
						7	423.7	2.5	426.2	2.200	0.000		
						8	429.9	2.5	432.4	2.200	0.000		
							<u>3348.1</u>		<u>3368.0</u>		<u>0.581</u>		
9	29-3	11.7	525	35.9	1.89	0	---	---	---	2.200	---	5.19	111
						4	1658	11	1669	2.073	2.120		
						8	<u>1681</u>	11	<u>1692</u>	2.140	<u>1.015</u>		
							<u>3339</u>		<u>3361</u>		<u>3.135</u>		
10	P-25	16.4	525	24.8	1.89	0	---	---	---	2.200	---	7.90	120
						4	1634	20	1654	1.979	3.655		
						8	<u>1582</u>	21	<u>1603</u>	2.106	<u>1.507</u>		
							<u>3216</u>		<u>3257</u>		<u>5.162</u>		
11	P-26	15.9	525	26.9	1.89	0	---	---	---	2.200	---	7.93	120
						4	1709	15	1724	1.995	3.532		
						8	<u>1687</u>	16	<u>1703</u>	2.080	<u>2.043</u>		
							<u>3396</u>		<u>3427</u>		<u>5.575</u>		
12	P-27	17.4	525	24.3	1.89	0	---	---	---	2.200	---	7.92	---
						4	1649	24	1673	2.130	1.172		
						8	<u>1685</u>	25	<u>1710</u>	---	---		
							<u>3334</u>		<u>3383</u>				

TABLE VI (continued)
COMPARATOR RUN CONDITIONS AND CALCULATIONS

Run No.	Catalyst	Wt gms	Temp Of	Space Velocity $\frac{\text{gms oil}}{\text{gm cat hr}}$	H. rate SFP ft ³ /hr	Time Hrs.	Wt oil before correction gms	Losses gms	wt oil after correction gms	Percent Sulfur	Sulfur removed gms	Nickel in Catalyst gms	Percent nickel sulfided
13	P-28	15.6	525	27.5	1.89	0	---	---	---	2.200	---	7.93	49.8
						4	1523	9	1532	2.093	1.638		
						8	1887	10	1897	2.173	0.512		
							3410		3429		2.150		
14	P-29	9.8	525	43.7	1.89	0	---	---	---	2.200	---	5.03	82.6
						4	1644	8	1652	2.100	1.652		
						8	1748	8	1756	2.165	0.615		
							3392		3408		2.267		
15	P-30	17.4	525	24.8	1.89	0	---	---	---	2.200	---	7.90	52.7
						4	1729	5	1734	2.120	1.387		
						8	1726	6	1732	2.149	0.883		
							3455		3466		2.270		
16	P-31	14.8	525	29.1	1.89	0	---	---	---	2.200	---	6.32	65.2
						4	1729	6	1735	2.105	1.648		
						8	1704	7	1711	2.165	0.599		
							3433		3446		2.247		
17	P-37	13.6	525	31.5	1.89	0	---	---	---	2.200	---	7.31	83.7
						4	1669	5	1674	2.079	2.025		
						8	1743	6	1749	2.125	1.312		
							3412		3423		3.337		

TABLE VI (continued)
 COMPARATOR RUN CONDITIONS AND CALCULATIONS

Run No.	Catalyst	Wt. gms.	Temp. °F	Space Velocity $\frac{\text{gms oil}}{\text{gm cat hr}}$	H ₂ rate STP ft ³ /hr	Time Hrs.	Wt. oil before correction gms.	Losses gms.	Wt. oil after correction gms.	Percent Sulfur	Sulfur removed gms	Nickel in Catalyst gms	Percent nickel sulfided
18	P-39-A	13.5	525	31.8	1.89	0	---	-	---	2.200	---	7.25	115
						4	1692	6	1698	1.994	3.500		
						8	<u>1732</u>	6	<u>1738</u>	2.140	<u>1.043</u>		
							3424		3436		4.543		
19	P-42	15.0	525	28.3	1.89	0	---	-	---	2.200	---	7.49	87.7
						4	1664	16	1680	2.051	2.503		
						8	<u>1694</u>	16	<u>1710</u>	2.137	<u>1.078</u>		
							3358		3390		3.581		
20	P-43	14.1	525	30.0	1.89	0	---	-	---	2.200	---	7.30	110
						4	1662	14	1676	2.009	3.200		
						8	<u>1694</u>	15	<u>1709</u>	2.131	<u>1.180</u>		
							3356		3385		4.380		
21	P-44	14.3	525	29.7	1.89	0	---	-	---	2.200	---	7.34	97.2
						4	1695	5	1700	2.055	2.465		
						8	<u>1688</u>	6	<u>1694</u>	2.116	<u>1.423</u>		
							3382		3394		3.888		
22	P-45	13.0	525	33.2	1.89	0	---	-	---	2.200	---	7.34	140
						4	1702	13	1715	1.964	4.045		
						8	<u>1729</u>	13	<u>1742</u>	2.111	<u>1.550</u>		
							3431		3457		5.595		

TABLE VI (continued)
 COMPARATOR RUN CONDITIONS AND CALCULATIONS

Run No.	Catalyst	Wt. gms.	Temp. °F	Space Velocity gms oil ag cat. hr.	H ₂ rate STP ft ³ /hr	Time Hrs.	Wt. oil before correction gms.	Losses gms.	Wt. oil after correction gms.	Percent sulfur	Sulfur removed gms	Nickel in Catalyst gms	Percent nickel sulfided
23	P-48	12.0	525	33.3	1.89	0	---	---	---	2.200	---	7.38	128
						4	1686	10	1696	1.995	3.476		
						8	<u>1726</u>	11	<u>1737</u>	2.103	<u>1.685</u>		
							3412		<u>3433</u>		<u>5.161</u>		
24	P-55-B	13.9	525	30.9	1.89	0	---	---	---	2.200	---	7.35	116
						4	1664	10	1674	2.007	3.231		
						8	<u>1753</u>	11	<u>1764</u>	2.120	<u>1.412</u>		
							3417		<u>3438</u>		<u>4.643</u>		

