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Trace elements balance in a refinery

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Abstract The trace elements balance is performed whenever the refinery processes a new type of oil. The goal of the balance is to find the distribution of the trace elements in the products and residues for the market. Also, the balance can warn about the accumulation of metals in the catalysts, this affecting their activity in time. This work presents the case study of a refinery processing a light and sulphurous oil with a medium concentration of trace elements. The study highlighted the following: the highest levels of concentration in feed and products are for Na and Si; in general, trace elements concentrate in heavier factions and residues and especially in the coke as a product or as deposited on calaysts; following the balance, heavy metals concentrate in the coke deposit on FCC catalyst in range of 53% for V to 83% for As; heavy metals concentrate in the gasoline hydrotreating catalyst in range of 7% for Ni to 87% for V.

Keywords: crude oil, trace elements balance, ICP-MS

1. Introduction

About half of the elements from the periodic table were found in the crude oil: carbon and hydrogen dominate, sulphur, oxygen and nitrogen are in percents and metals in trace, mg/kg or µg/kg. A large variety of trace elements was reported in different sources but the most complete list [1] include 28 of them. The most frequent is Na, then Si but among the transitional metals, Ni and V are more abondant. The study of the metals in crude oil gives clues about the origin and age [2,3]. Also, the study of metals content in crude oil and their distribution in refinery products performed whenever the refinery processes a new type of oil, would give information about the processability of the oil and the value of the products on the market. Moreover, the metal balance in an oil refinery when the quality of feed changes will provide data about accumulation in catalysts with impact on their deactivation, this allowing to preview the length of processing cycle.

The present work is an example of trace elements balance in the refinery in order to conclude on the processability of that oil.

2. Experimental

The refinery processes a light (d_{15}^{15} = 0.8512) and sulphurous (1.05 %wt) oil. The balance is performed in a typical processing day, using mass balance of feed and products and trace elements concentration in each of them.

The main trace elements in the oil have been monitored: V, Ni, Zn, As, Na and Si. Their concentration has been analysed by a spectrometric method. Due to expected low concentration of some metals, the ICP-MS method was prefered. It was used a Agilent 7500ce aparatus. Detection limits were: 0.01130 µg/L for V, 0.07522 µg/L for Ni, 0.09363 µg/L for Zn, 0.02369 µg/L for As, 0.2887 µg/L for Na and 0.2389 µg/L for Si.

The standard methods used for sample preparation were ASTM D-5184/1995 [4], ASTM D 4951/1996 [5] and ASTM D5600/1998 [6] based on acid digestion of the ash in such conditions that the losses of volatile metallic compounds were minimized. Direct introduction of petroleum product in plasma, dilluted or not, was avoided due to the matrix effect.

Material balance on each process for every metal was performed with Eq.1, using the raw flows

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[kg/day], product yields (%) and metal content [mg/kg]:

$$(raw\_flow) \times (metal\_content) = \sum(product\_flow)\times(metal\_content) + losses \quad (1)$$

Since losses were under 0.5% in each process, the mass balance closed satisfactorily for each element. Data obtained with Eq.1 served to calculate the distribution of trace elements in products of the processes and then to observe the tendency of metals to concentrate in one product, or another or on catalysts

3. Results and Discussions

The results of metal analysis in raw materials and products of the refinery give information about the content of trace elements in petroleum product and they are shown in **Table 1**. The concentration are expressed as mg/kg (ppm wt)

Table 1. The trace metals concentration in raw materials and products, mg/kg

Raw or product	Daily quantity, t	As	V	Si	Ni	Zn	Na
Atmospheric and Vacuum Distillation of Crude Oil							
Crude oil	11463	0.21	2. 5	0.66	1.1	1.2	12
Light naphtha	1182	0.0046	0.0005	0.79	0.01	0.024	0.66
Heavy naphtha	1001	0.038	0.0008	0.47	0.013	0.028	0.6
Jet fuel	1186	0.049	0.13	0.38	0.011	1.1	3.1
Gas oil	2805	0.16	0.22	0.31	0.1	1.2	12.75
Vacuum distillate	3096	0.22	0.66	0.56	0.12	1.5	11
Vacuum residue	2153	0.53	12. 00	1.41	5.5	2	29
Naphtha Hydrotreating							
Heavy naphtha in line	1170	0.0046	0.0005	0.79	0.01	0.024	0.66
Naphta from tank	1139	0.018	0.0006	0.44	0.013	0.028	0.6
Coke gasoline	238	0.13	0.001	1.5	0.017	0.037	1
Mixed Feed	2547	0.022	0.0006	0.70	0.012	0.027	0.66
Hydrotreated gasoline	1514	0.014	0.0001	0.37	0.013	0.02	0.52
C5-C6 cut	605	0.0005	0.0001	0.1	0.014	0.026	0.63
Gas C2-C4	428	N/A	N/A	N/A	N/A	N/A	N/A
Fluid Catalytic Cracking							
Hydrotr. vac. distillate	3712	0.21	0.61	0.52	0.011	1.01	9.8
FCC light gasoline	1545	0.0022	0.0006	0.063	0.02	0.033	0.57
FCC heavy gasoline	111	0.039	0.009	0.11	0.037	0.062	3.5
FCC light gas oil	501	0.14	1. 3	0.26	0.11	1. 4	8.1
FCC heavy gas oil	282	0.18	1. 4	5.2	0.13	1. 5	8.8
Gas+coke on catalyst	1273	N/A	N/A	N/A	N/A	N/A	N/A

Coke Unit							
Vacuum residue	2029	0.54	12	1.41	5.5	2	29
Coke gasoline	238	0.13	0.001	1.52	0.017	0.037	1
Light coke gas oil	612	0.25	1. 5	0.23	0.12	1.03	5.9
Heavy coke gas oil	596	0.19	1. 2	0.54	0.089	1. 3	10
Petroleum coke	583	1.43	40.53	3.43	19.26	4. 8	88.1

From Table 1, one can see that, for every process in the refinery, the metal content in products and residuues increases with the boiling temperature of these; in Table 1 products of each process are in range of increasing boiling temperatures. The metals level is higher in feed and products from distillation of crude oil and Fluid Catalytic Cracking (FCC): ppm, and even higher in Coke unit products (dozen of ppm). Na is the main metal in all petroleum products, V, Zn and Ni are second third and fourth in the raw and products. Ni and V concentrate in residues and are also present over 1 ppm in gas oils. Only Zn is found in FCC gasoline in concentration over 1 ppm.

Following the mass balance on each process for every metal (Eq.1), the distribution of metals in the products was calculated.

In **Fig. 1**, the distribution of As in products of different processes is shown.

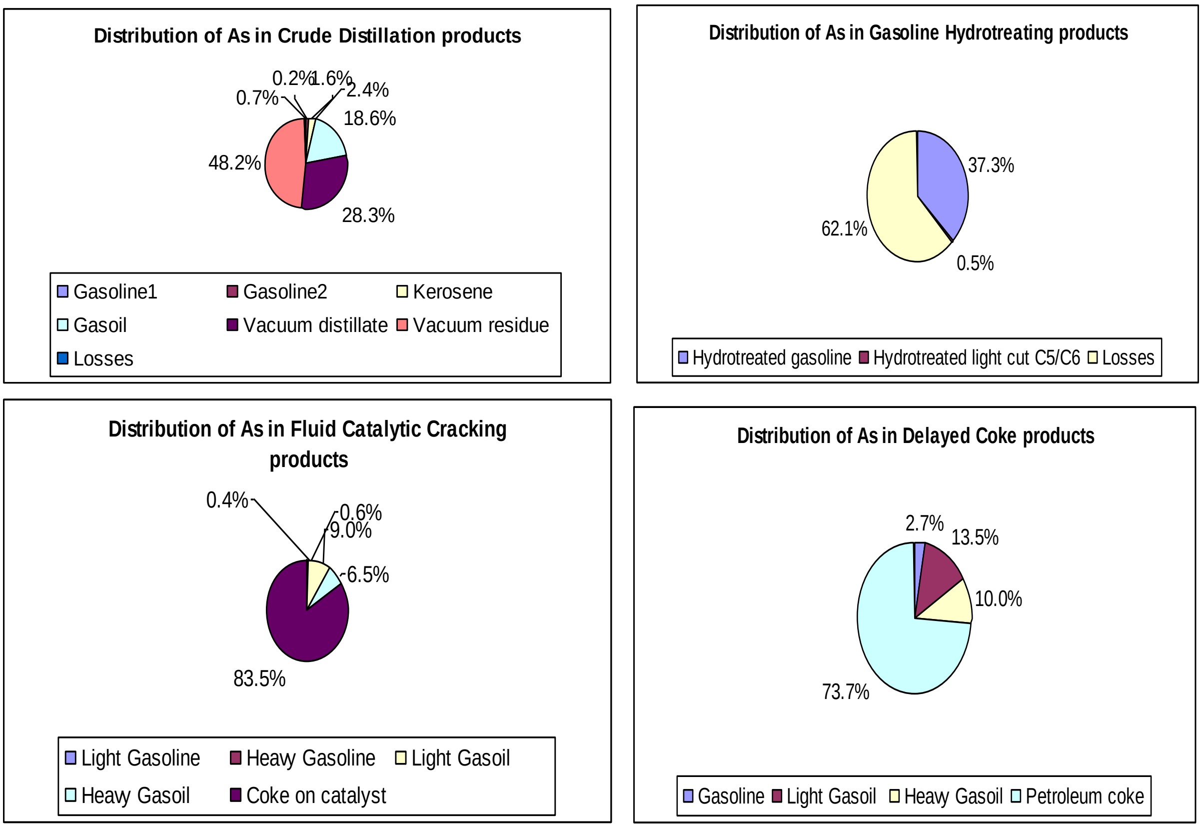

Fig.1. Distribution of As in the refinery products

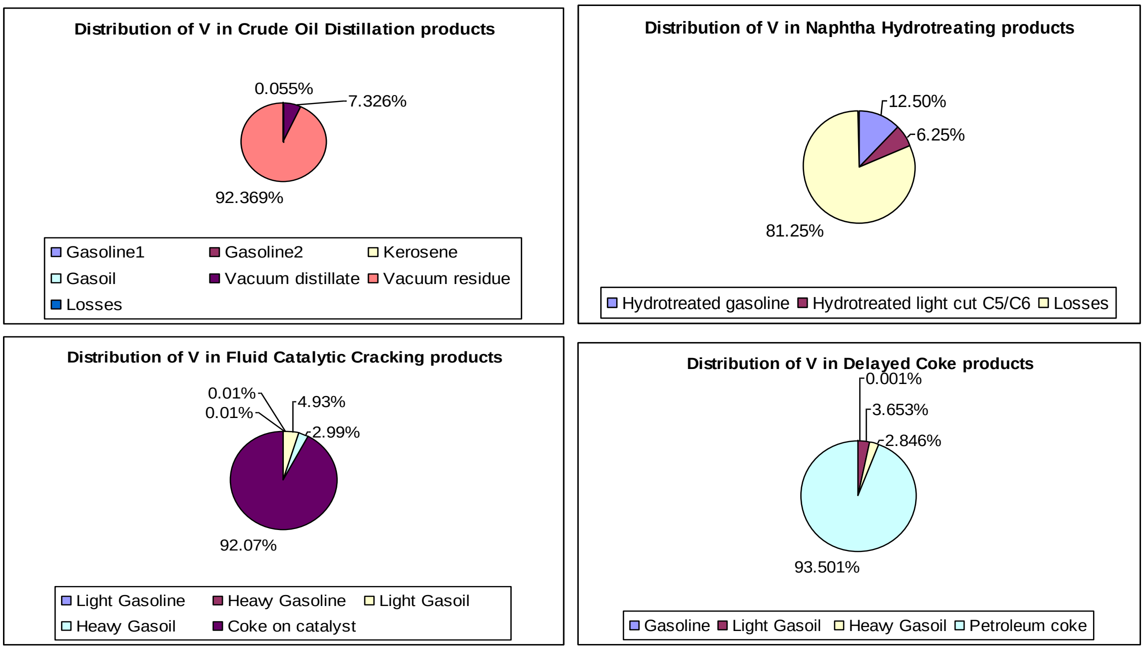

Fig.2. Distribution of V in the refinery products

As seen, As accumulates in residues (48.2% in vacuum residue proceeding from crude oil, 73.7 % in petroleum coke). A good share concentrates on catalysts: 83.5% for all the As in the feed of Fluid Catalytic Cracking is found on the catalyst and 62.1% of that in Naphtha Hydrotreating process is removed from naphtha, but one can't say how much is on catalyst or gone with fuel gas as volatile compounds; the analysis of the metals in hydrotreating catalyst is pointless since the catalyst already contains a high level of metals so small adding due to the feed is not detectable.

As seen in **Fig. 2**, a similar tendency was noticed for the Vanadium but this one accumulates over 90% in residues and on FCC catalyst. Accordingly, removal of V from naphtha during hydrotreating is 81.25% comparing with Ni (62.1%)

In **Fig. 3**, the distribution of Ni seems similar to that of As and V, with a significant difference: Ni is accumulating more in hydrotreated gasoline than previous metals (64.4% comparing with 37.3 %As and 12.5% Ni), this meaning that the share for hydrotreating catalyst plus losses with fuel gas is much smaller (7.8%). The conclusion is that removal of Ni from naphtha during hydrotreating is less effective than for As and V.

In **Fig. 4**, the distribution of Zn is shown. Zn is accumulating in residues and catalyst like As, Ni, V but in smaller measure (e.g. Zn share in vacuum residue is 33.8% since for As the share is 48.2%, for V it is 93.4%, and 93.6 % for Ni. Also, Zn is found in gasolines in very small proportion: 0.1-0.2% in all the processes very much alike with the other metals. Differently, the Zn is distributed rather uniformly in naphtha hydrotreating products, so the removal of Zn from naphtha is not very effective during the hydrotreating process.

Silicon (**Fig. 5**) accumulates mostly in residues (petroleum coke and coke on FCC catalyst) but an important share is found in distillated products too (12.2% in heavy gasoline from crude oil distillation, 31.4% in hydrotreated gasoline, 5% in light gasoline and 76% in heavy gasoline from FCC); however, this doesn't affect the quality of gasoline pool.

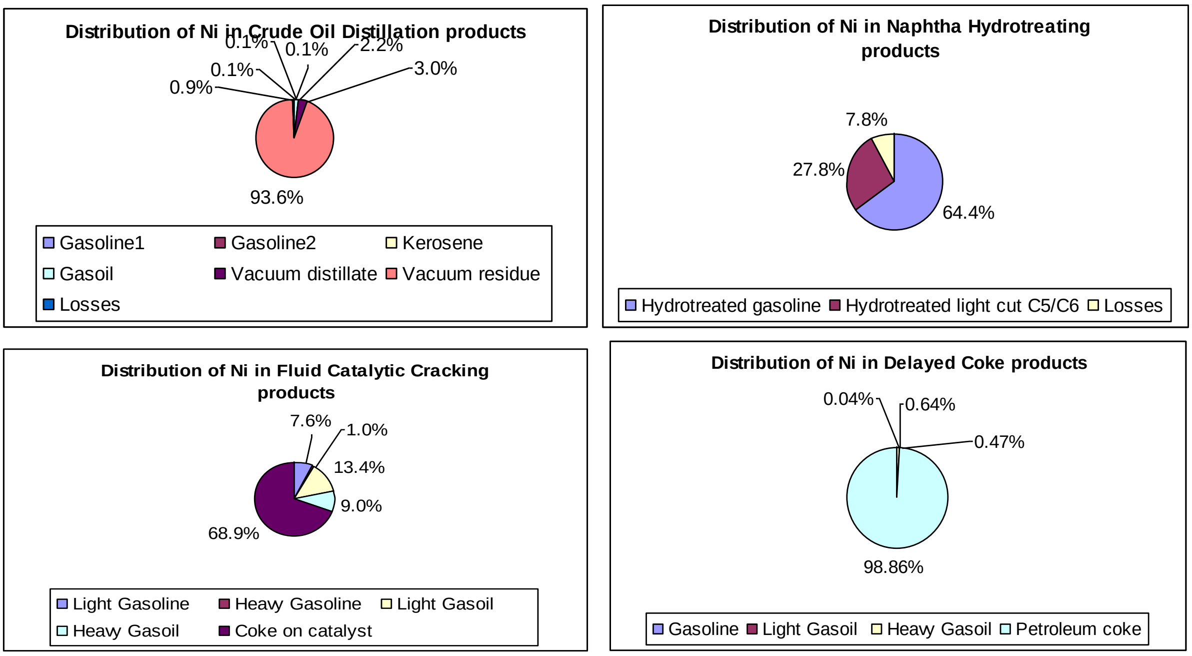

Fig.3. Distribution of Ni in the refinery products

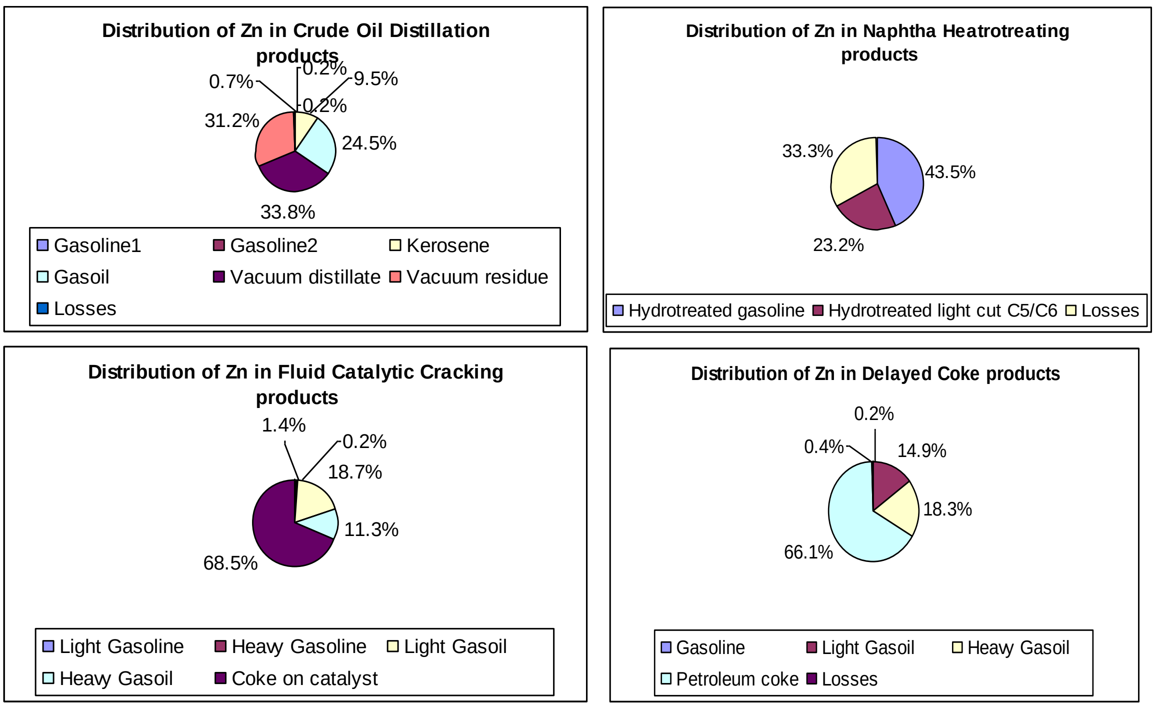

Fig.4. Distribution of Zn in the refinery products

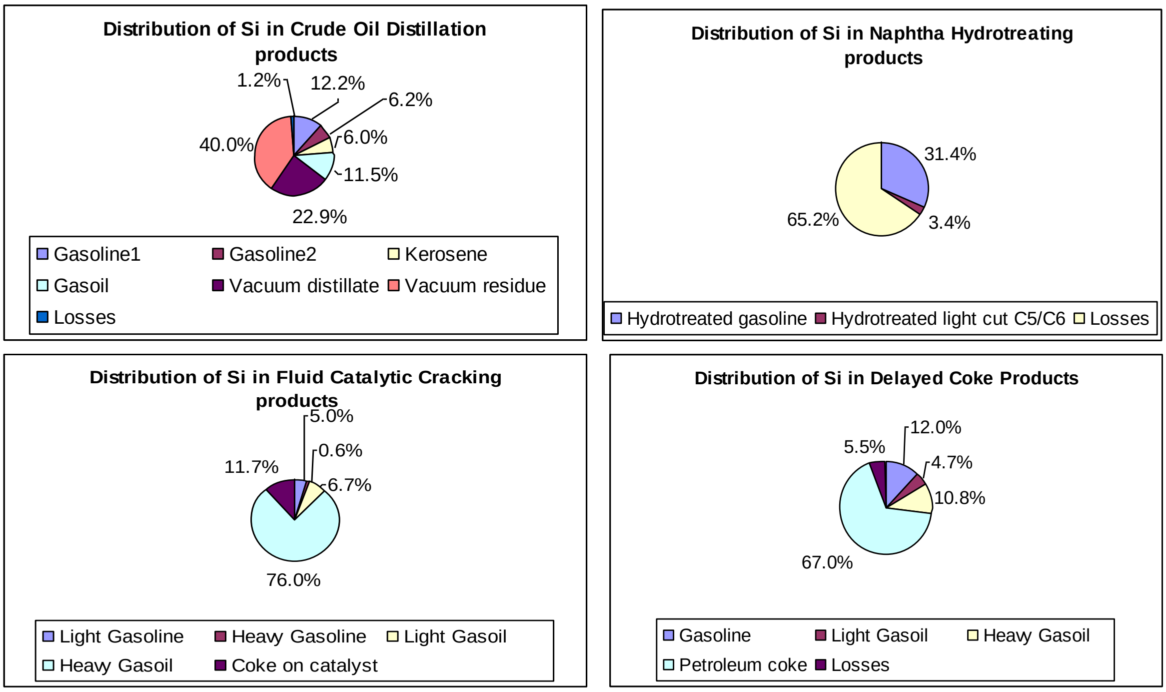

Fig.5. Distribution of Si in the refinery products

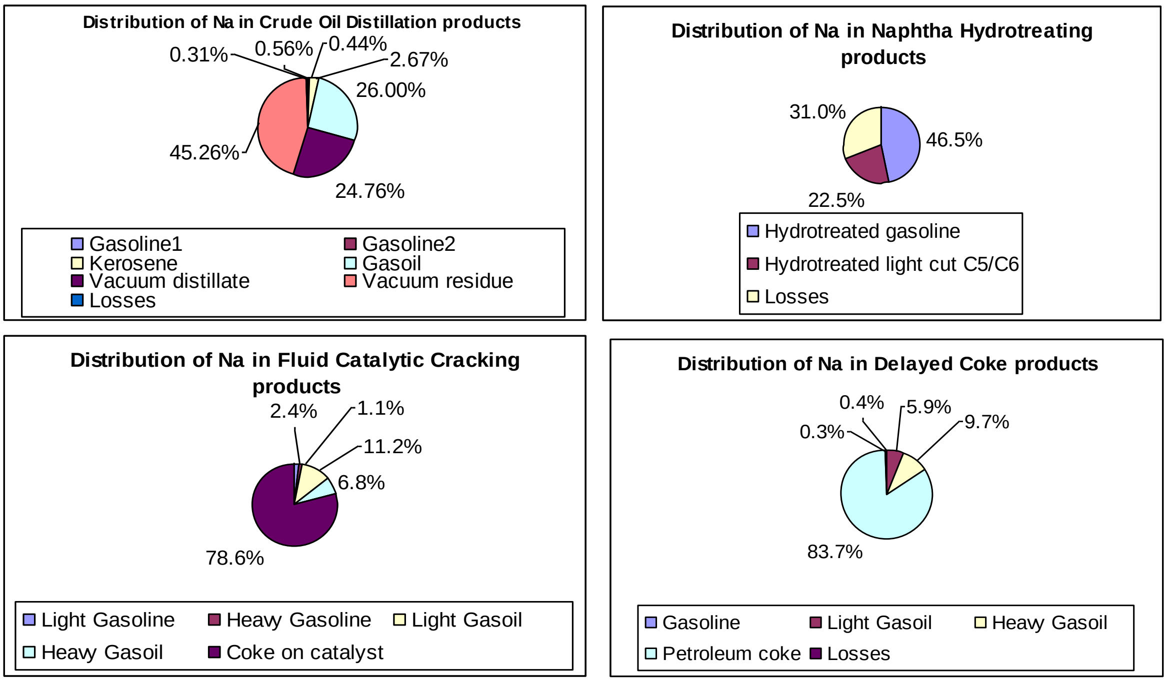

Fig.6. Distribution of Na in the refinery products

Natrium (**Fig. 6**), the most frequent metal in crude oil, is accumulating in residues as all the other trace elements but also in gas oil (26% in crude distillation gas oil, 11.2% in light and 6.8% in heavy gas oil from FCC and 9.7% in the gas oil proceeding from Delayed Coke unit). Like Si, it is found also in gasolines in important shares but Na as Si are harmless for the gasoline and gasoil quality.

4. Conclusions

Mass balance is an useful method for predicting the trace elements level in the products proceeding from a certain crude oil. Also, the metal balance can serve to measure indirectly the quantity lost in emissions and deposed on catalysts.

This study was performed in a refinery processing a light and sulphurous crude oil. The conclusions after the metals balance were the following:

- In Crude Oil Distillation process, all the metals concentrate in vacuum residue but an important share is also in the vacuum distillate; in gasoline, less than 0.1% of the heavy metals (As, Ni ,V) concentrate and in kerosene only As represents more de 1% of the total quantity entered with the crude; due to the high flowrate of gasoline, the level of As in the naptha is in range of ppb;
- In Naphtha Hydrotreating process, As is removed in proportion of 67.3%, 85.3% of Ni is removed but only 7.4% of Ni is removed; the concentration level of heavy metals in hydrotreated gasoline is: 14 ppb for As, 13 ppb for Ni and 0.1 ppb for V; this level of concentration affects in small measure the activity of the catalyst in the downstream process: Reforming Gasoline;
- In Fluid Catalytic Cracking process, metals accumulate in the coke deposit on the catalyst, except Si concentrating in heavy gas oil (76 %);
- During Delayed Coke process, all metals accumulates in the petroleum coke; in distillates, the concentration level of heavy metals Ni, V and As is under 1 ppm and only V is slightly over 1 ppm in gas oil.

5. References

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[1] J. Sanbayar, D. Monkhoobor, B. Avid, Advances in Chemical Engineeering and Science **2**, 113 (2012)
[2] L. Lopez, S. Lo Monaco, Fuel, **83**, 365 (2004)
[3] F. Galarraga, K. Reategui, A. Martinez, M. Martinez, J.F. Llamas, G. Marquez, Journal of Petroleum Science and Engineering, **61**, 9 (2008)
[4]***ASTM D-5184/1995 "Aluminium and Silicon in Fuel Oils by Ashing, Fusion, ICP-AES and AAS Spectrometry"
[5] ***ASTM D-4951/1996 "Additive Elements in Lubricating Oils by ICP-AES"
[6] ***ASTM D-5600/1998 "Standard Method for Trace Metals in Petroleum Coke by Inductively Coupled Plasma Atomic Emission Spectrometry"

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