Theoretical and Experimental Evaluation of Particle size Effect of Iron , Cobalt ,and Nickel Powders Suspended in Al Dura oil on XRF Intensities

Abdulhadi K.Jedran*

Abstract :

Iron , Cobalt , and Nickel powders with different particle sizes were subjected to sieving and He-Ne laser system to determine the particle size . 1wt% from each powders was blended carefully with 99wt% from Iraqi oil . Microscopic examination were carried for all samples to reveal the particle size distribution . A Siemens type SRS sequential wavelength dispersive(WDS) X-ray spectrometer was used to analyze all samples , and the XRF intensity were determined experimentally and theoretically for all suspended samples , Good agreement between theoretical and experimental results were found .

Introduction:

X-Ray Fluorescence (XRF) is capable of measuring fine particles as well as plate metal sample , however , it is limited by the depth from which the X-rays are capable of exciting the sample . This leads to a particle size effect [1] . It is difficult to obtain successful X-ray control of materials without some understanding of the effect of the two most important variables influencing X-ray intensities in suspended samples namely particle size and homogeneity [2,3] . In addition its use of organometallics and dissolved metals , XRF has been applied to suspended metal particulate in oil lubrication system [4].

Theoretical part :

When X-ray passes through the object being tested , the signal is attenuated by scattering and absorption according to Beers law :

$$I = I_O e^{-\mu\chi} \text{------------(1)}$$

Where IO: the initial intensity .

       I: the final intensity .

μ : the attenuation coefficient (cm-1) .

χ : the length of X-ray path (cm) .

But the actual volume of sample which can contribute to the measured fluorescent radiation is independent upon the effective penetration depth of the measured wave length [5,6] . This in turn supports need for completely homogenous specimen . Since if for instance compositional variation in depth are present if we consider a powder sample containing the element of interest in spherical particles of a uniform diameter D , then at any depth of χ from the surface there are likely to be N particles , where N is proportional to the concentration of the element . If the original particle diameter is reduced to (D/2) , then at the same depth χ there will be (8N) particles , if the particles are cubic in shape then the particle size reduction again results in an eight fold increase in number and can be described as a lateral displacement of the lower half of the cubic . The exciting radiation is again absorbed by the matrix until it reaches the surface and is measured .

* Technology ,University, school of Applied science ,Iraq, Baghdad.

Assuming the average depth of particles is the same for the different particle size , then the total matrix absorption is virtually independent of particle size . It is evident that for
cubic particles reducing the dimension of a side by two is equivalent to
exposing twice the original area of the material being measured at a half of the original thickness . In the spherical particle the same is true since the surface area of a sphere is proportional to the diameter squared [7,8] . It is a well known fact that the intensity of a characteristic line emitted by a thin layer of material increases the thickness is increased up to a point which we will define as infinite thickness , value any increase in thickness will result in no observable gain in characteristic signal from the sample [9] . The relation ship between the fluorescent intensity from the same sample which of infinite thickness can be shown to be as follows [7,10] .

$$(I_x/I_\infty) = 1-EXP(-a\rho\chi c) \text{ -----------(2)}$$

Where I_x and I_∞ are the intensities of fluorescent radiation per square centimeter leaving samples of thickness χ and ∞ respectively .
a : the absorption parameter .
ρ : the density of sample .
χc: the critical thickness of sample .

And $a=\mu_i \csc\theta_i +\mu_e\csc\theta_e$ -----------(3)
Where μ_i and μ_e are the absorption coefficient for incident and emergent X-ray respectively . θ_i and θ_e are the incident and emergent analysis respectively . The effect of inhomogeneity of particle size (Fig.2.1) within samples of one compound was studied , the smallest size show to yield highest intensities [11].
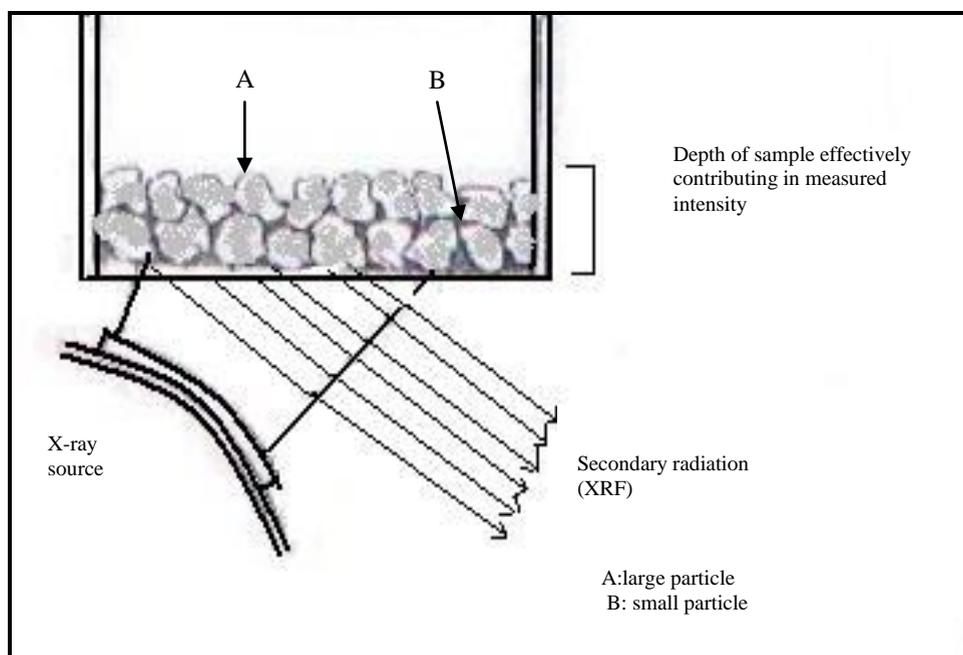

Depth of sample effectively contributing in measured intensity

X-ray source

Secondary radiation (XRF)

A:large particle
B: small particle

Fig.(2.1) in homogeneity of particle size effect [11] .

Theoretical calculations :

In order to determine infinite thickness from the equation(3) we arbitrarily choose a value of 0.99 for the ratio of (Ix/I∞) . We can define particle size in terms of the infinite thickness value , and by using the equation(3) can be calculated the absorption parameter (a) from the data as shown in Table (3.1) . The values of μi and μe were determined by using soft ware program [12] , θe values from ref [13] , and θi =52.5 for XFR system which was used in this work .

Table (3.1) The values of absorption coefficients and diffracted angles of element used in this work .

Element	μ_i (cm²/g) at operated energy(0.41°A)	μ_e (cm²/g) at K_α line	θ_e	a (cm²/g)	χ_c (μm)
Iron	7.09	71.04	57.46	93.202	62.50
Cobalt	7.86	78.47	52.74	108.497	47.69
Nickel	8.65	91.26	48.60	132.313	39.11

Now the critical area for Iron , Cobalt , and Nickel can be calculated by using the critical thickness (table 3.1)and considered the shape of particles is spherical , and these values equal to 1.23×10^{-4} cm2 for Fe , 7.14×10^{-5} cm2for Co , and 4.8×10^{-5} cm2 for Ni , and the another step represents calculate the real area by using the measured average particle size as shown in tables (3.2) , (3.3) , and (3.4) for Fe , Co , and Ni respectively .

Table (3.2) Particle size , area , and number of times of real area increased over critical area of Iron samples .

Average particle size (cm²)	Area (cm²)	No. of times of real area increased over critical area
0.022	0.00152	12.39
0.024	0.00181	14.74
0.030	0.00282	23.04
0.032	0.00321	26.21

Table (3.3) Particle size , area , and number of times of real area increased over critical area of Cobalt samples .

Average particle size (cm²)	Area (cm²)	No. of times of real area increased over critical area
0.0055	0.000094	1.330
0.0060	0.000113	1.580
0.0065	0.000132	1.860
0.0075	0.000176	2.473

Table (3.4) Particle size , area , and number of times of real area increased over critical area of Nickel samples .

Average particle size (cm²)	Area (cm²)	No. of times of real area increased over critical area
0.0075	0.000176	3.680
0.0085	0.000227	4.72
0.0105	0.000346	7.210
0.0115	0.000415	8.650

Now we can calculated the theoretical relative intensity (I/I$_O$) for all suspended samples as shown in table(3.5) .

Table(3.5) Theoretical relative intensity for Fe , Co , and Ni suspended in Iraqi oil .

Samples	Theoretical relative intensity
Fe	0.729
	0.698
	0.617
	0.593
Co	0.981
	0.974
	0.965
	0.946
Ni	0.909
	0.880
	0.820
	0.791

Experimental part :
1- Sample preparation :

The average particle size measurements for Fe , Co , and Ni powders were conducted by using different sieving of range (20-300μm) and subjected to He-Ne laser system of wave length 632 nm and power of 1mwatt to determine the experimental

average particle size for Fe , Co and Ni powders with more accurate .The different particle size of Fe , Co and Ni powders were blended with Al Dura oil of SAE=40HD ,flash point = 236 , viscosity at 100 oC= 15 centistock , and pour point at -9 oC [14] . 1wt% from each particles and 99wt% from oil were blended carefully manually and by using ultrasonic generator .Microscopic examination was conducted for all suspended samples to reveal the particle size distribution in oil matrix.

2 -XRF intensity measurements :

The XRF system was operated at fixed operation conditions of 30KV and 17mA . All suspended samples were placed in liquid samples container and then fitted to X-ray fluorescence system to conduct XRF intensities of Fe Kα ,Co Kα , and Ni Kα lines in (count/10s) and averaged to (count/s) . to evaluate the effect of particle size on XRF intensity .

Results and discussion :

Figures (5.1) , (5.2) , and (5.3) represents the microscopic examination of 1 wt% from Fe , Co , and Ni with different particle size suspended in oil .
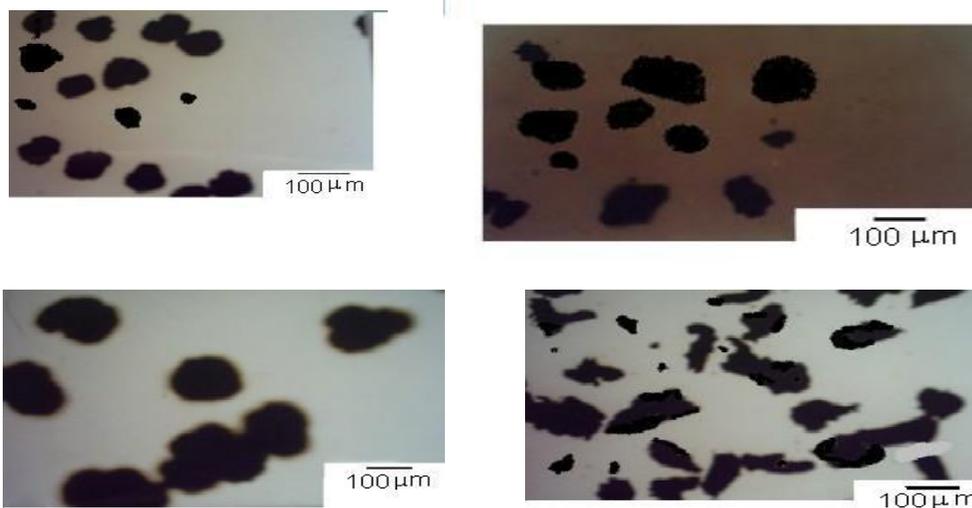
Figures (5.4) ,(5.5) , and (5.6) represents the XRF theoretical relative intensity and real intensity (which was calculated as the peak intensity of suspended samples to the peak intensity for the pure sample) for Fe , Co and Ni powders suspended in oil as a function of particle sizes . These figures exhibited the results of XRF measurements which determined theoretically and experimentally for different particle size . Particles of smallest size shown to yield highest intensities while particles which has large particle sizes shown to yield lowest intensities for all specimens , the behavior of intensity curve due to that the increase in intensity was attributed to a decrease in voids of the specimen surface with the reduction in particle size , and this leads to the excitation area will be large . Some differences between the theoretical intensity and the real intensity due to statistical errors which were happen in XRF measurements and to electrical noise and may be due to sample preparation method . These results agreement with some references [2,8] .

Fig (5.1) Microscopic photograph of Iron powder suspended in oil at different particle size . X100
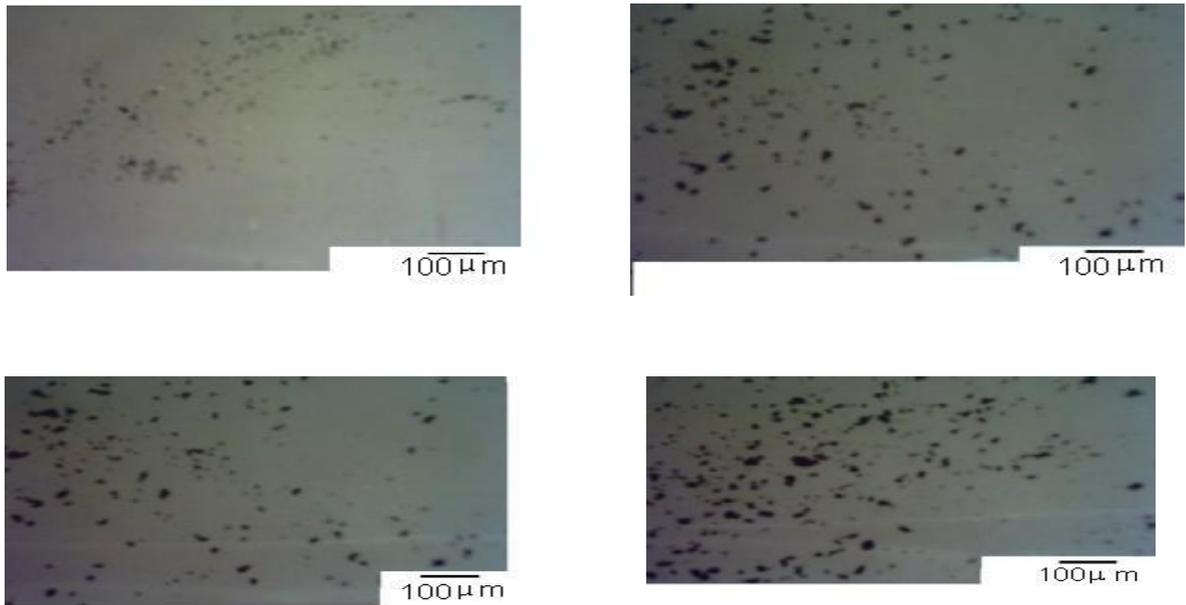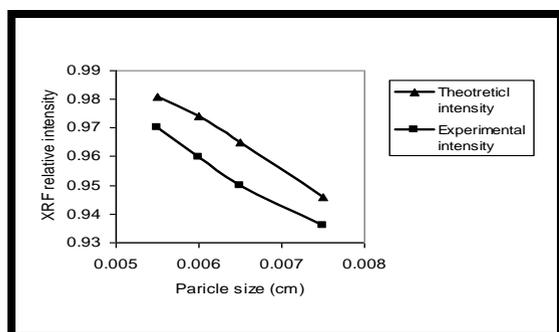
Fig.(5.2) Microscopic photograph of Cobalt suspended in oil with at different paticle size .X100
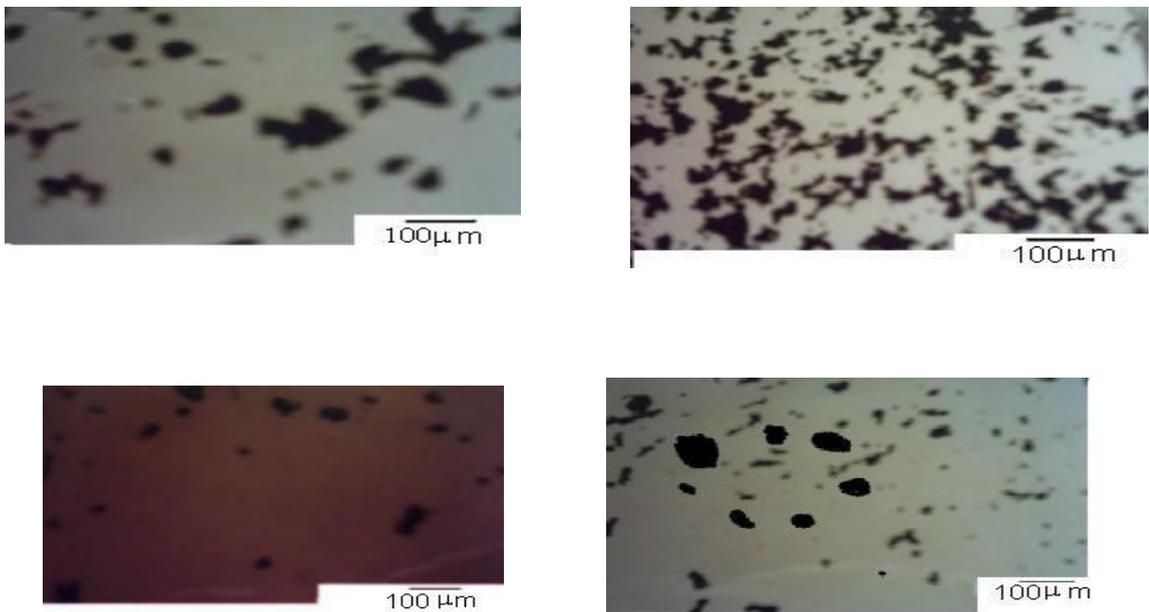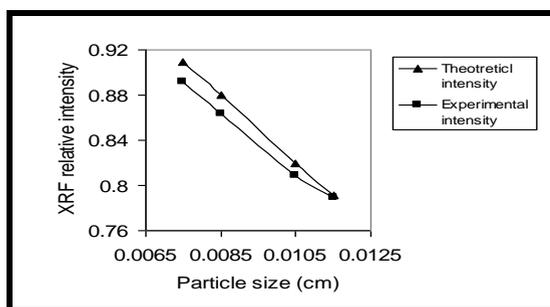

Fig (5.3) Microscopic photograph of Nickel powder suspended in oil at different particle size
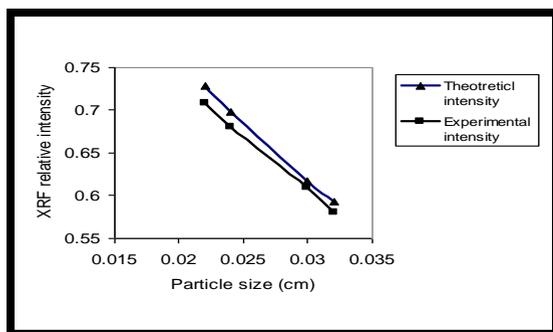
Fig.(5.4) XRF relative intensity as a function of particle size for Fe powders suspended in Iraqi oil .

Fig.(5.5) XRF relative intensity as a function of particle size for Co powders suspended in Iraqi oil .

Fig.(5.6) XRF relative intensity as a function of particle size for Ni powders suspended in Iraqi oil .

Conclusions:

- From information gained in the present research certain conclusions may be draw regarding the X-ray fluorescent behavior of particles in oil suspension . Iron of 0.022 cm in size yield about 71% the intensity of a real sample , an increase in fluorescence in size up to 0.032 cm results in a decrease in fluorescent intensity by at least 20% . Cobalt of 0.005 cm in size yield about 97% the intensity of a real sample , an increase in fluorescence in size up to 0.0075 cm results in a decrease in fluorescent intensity by at least 5% . Nickel of 0.0075 cm in size yield about 90% the intensity of a real sample , an increase in fluorescence in size up to 0.0115 cm results in a decrease in fluorescent intensity by about 12% .

- Good agreement between the theoretical and experimental relative intensity for samples was found .

References :
1. Humphrey,G.R.; and Darrel, B.C.;(1998). The path to affordable long term failure warning *,the XRF-monitor. international condition monitoring Conference*, Alabama .

2. Bernstien, F.; (1963).Advances in X-ray analysis . published by General electric company . *Vol.6 ,* pp436-455 Wisconsin USA .

3. Tertian, R.; and Claisse,F. (1996). Principles of Quantitative X-ray fluorescence Analysis Hyden & sons Ltd.London .

4. Whitlock,R.R.;(1997). Filter debris analysis using XRF *.proceeding of the 51st meeting of the society for machinery failure prevention technology (MFPT) .Virginia* .

5. Jenkin, R.; (2000).X-ray technique . *Encyclopedia of Analytical chemistry* pp13269-13288 , John wiley & sons Ltd , chichester .

[6] Jenkins, R. ; and Devries, J.L. (1970). Practical X-ray spectrometry *Second edition* , printed in Great Britain by Hazell Watson-Viney Ltd.

7. Havrilla, G.J.;(1997). X-ray fluorescence spectrometry. *Pretice Hall PTR , Newjersey.*

8. Gunn, E.L.; (1968). Advances in X-ray analysis . *Vol.11* , pp165-176.

9. Darrel, B.C.; Gray, M.; and Whitlock, R.R.; (1996) . advances in X-ray analysis. *Vol.40* .

10. Mark,B.; Berry, P.; and Voots, G.; (1995). Spectrace 9000 Field portable XRF . *Congress on X-ray Analytical methods . pp1-6*

11. Graham, B.J.; and Thomas, N. (1975). " An introduction to Physics for radiologists technologists . Newyork .

12. Hubbel, J.; (1999).X-com microsoft program . USA .

13. White, G.W.; (1970).ASTM DATA SERIES DS 37A. .

14.Marketing specification of Iraqi petroleum production product.; (2000)

التقييم النظري والعملي لتأثير حجم الجسيمات لمساحيق من الحديد والكوبلت والنيكل عالقة في الزيت الدورة على شدة تألق الأشعة السينية .

عبد الهادي كاظم جدران*

*الجامعة التكنولوجية / قسم العلوم التطبيقية

الخلاصة:

مساحيق من الحديد والكوبلت والنيكل بمختلف الحجم الحبيبي أجريت عليها قياسات بواسطة الغرابيل وليزر الهليوم – نيون لإيجاد الحجم الحبيبي . (1wt%) من هذه المساحيق خلطت بعناية مع (99wt%) من الزيت العراقي . تم إجراء الفحص المجهري لكل العينات لمعرفة توزيع الجسيمات في الزيت . تم استخدام منظومة XRF نوع Siemens/srs-200 بمطياف للأشعة السينية المعتمد على تقنية تفريق الطول الموجي(WDS) لجميع النماذج. أجريت القياسات العملية والنظرية لشدة تألق الأشعة السينية لجميع العينات ووجد أن هناك توافقاً جيداً بين النتائج العملية والنظرية .