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Optimizing the Production of a Dense Magnetite-Ilmenite Blend with Lower Radioactivity

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Abstract

Heavy minerals proved to be a good candidate as an additive to concrete to produce shielding material. The higher the density is the better the shielding properties. In this study, the heaviest two minerals of the black sand beneficiation products; namely ilmenite and magnetite, were in preparing a mixture with a high specific gravity. However, such minerals in black sand are known by their radioactivity, thus, the radiation activity of each mineral was determined. in addition, the statistical design was used to indicate the importance of the mixture on the produced density and radioactive concentration. Furthermore, the resulting mixture was optimized to produce a mixture with the highest density and radioactive concentrations that do not exceed the standard limits. The results indicated the higher the content of both minerals is the higher the density. On the other hand, the radioactive activity of ilmenite is found to exceed the allowable limits contrary to magnetite which has a lower activity than standard values. Using the optimization process generated eight mixtures with a specific gravity between 4.7-4.8 and radioactive concentrations of 16, 15, and 58 Bq/kg for ^{226}Ra, ^{232}Th, and ^{40}K, respectively

Keywords: zircon; magnetite; concrete; shielding; radiation activity.

Introduction

Black sands are an excellent source of several economic minerals [1-2]. Among these minerals are ilmenite, rutile, magnetite, zircon, and monazite. Numerous previous studies focused on the study of the black sands' mineralogical component and their upgrading to achieve the highest level of their economic values [3-5]. These minerals in black sand are known also by the radioactive nature of them [6-7].

Recently, heavy minerals were used to produce heavy concrete which can be used for a specific purpose such as shielding against different types of rays [8-10]. Among these heavy minerals that can be used in heavy concrete production are magnetite and ilmenite [11-12]. Although both minerals are present in the black sand and have a reasonably high specific gravity, their radioactive nuclides concentration of these minerals is questionable. Previous studies on black sand minerals indicated that not all the minerals in black sand have a high radioactive concentration [13-15]. On the other hand, various studies focused on the environmental impact and associated hazards of using black sand minerals especially radioactive ones as building and construction materials [16-18].

Therefore, in this study, two minerals of the heaviest minerals were chosen to prepare a mixture that can be added to produce heavy concrete with reasonable and allowable radioactive limits. The statistical design of the experiment was used to find such a mixture using a factorial design. The analysis of variance was used to indicate the significance of each factor as well as the interaction between factors. The optimization techniques were used to find the possible situations or solutions that can produce the required mixture of the highest density and lies in allowable radioactivity limits.

Experimental

2.1 Materials

Zircon and magnetite are representative samples from concentration products of several beneficiation steps of gravity, magnetic, and electrostatic separations. The studied minerals were obtained from The Black Sand Company in Egypt.

2.2 Methods

2.2.1. Chemical composition - XRF technique

X-ray fluorescence (XRF), S-8 Tiger Bruker XRF Spectrometer, Bruker, Germany, is used to define the chemical composition of studied samples.

2.2.2 Density measurement

Ultrapyc 1200e Automatic Gas Pycnometer (Quantachrome Instruments, USA) was utilized to measure the mineral's density using a highly-purified nitrogen gas. The system resolution is $1x10^{-4}$ g/cm^3.

2.2.3 Radiological activity measurements

The two minerals were dried at 100 °C in a tightly sealed oven for 24 h to eliminate the contained moisture. Then, the minerals were kept in tightly sealed polyethylene Marinelli containers and left for 28 days before the radiological activity measurements [14, 19].

The radiological activity was measured by Sodium Iodide (NaI (Tl)) scintillation detector (Bicron) with a 3″×3″ crystal hermetically sealed with an aluminum-housing photomultiplier tube. To avoid the effect of induced X-rays and background radiation, the detector is placed in a hollow cylindrical lead chamber with a 6 mm-thick copper internal liner.

Uranium and thorium are alpha, not gamma, emitters so, they are indirectly measured using specific gamma lines emitted by their daughters [14].

The radioactivity concentrations (Ac) of; ^{226}Ra, ^{232}Th, and ^{40}K in (Bq/kg) which are contained in the studied samples were calculated, as shown in Eq. 1 [14-15], based on; the count rate of the selected ROI, C_s, in (count/sec), the corresponding background count rate, C_b, in (count/sec), the selected gamma line branching ratio, Iγ, in (%), the detector efficiency, ε, in (%), and the mass of the sample, M_s, in (kg).

$$Ac_{Ra,Th,or\ K} = \frac{C_s - C_b}{\varepsilon \cdot I_\gamma \cdot M_s} \quad (1)$$

The lower detection limit of ^{226}Ra, ^{232}Th and ^{40}K are 0.4 and 0.6 ppm and 0.1% respectively and the expected measurements' errors range between 5 - 15 %.

2.2.5. Statistical analysis

The 2^2 factorial statistical design of the experiment with three central points was used to find the best mixture of zircon and magnetite that achieve the higher density possible with permissible radioactive concentrations using an optimization tool. Table 1 shows the levels of the studied minerals. Different combinations of mineral percentages were run. The density and the radioactive concentration were used as responses. The Design-Expert software, Stat-Ease, Inc., Minneapolis, USA was used for statistical analysis and optimization of the responses in terms of the studied factors within a 95% confidence interval.

Table 1 The levels of factors

Factors		Levels		
		Low (-)	Mid (0)	High (+)
A	Magnetite, %	0	25	50
B	Zircon, %	0	25	50

Results and Discussion

3.1. Chemical compositions and densities

Table 2 shows the complete chemical composition of zircon and magnetite. Two minerals have considerable percentages of heavy elements such as titanium (^{48}Ti), iron (^{56}Fe), and/or zirconium (^{91}Zr). Zircon has the highest density, 5.23 g/cm^3, along with having a considerable amount of zirconium oxide, ZrO_2, which equals about 58%. Magnetite, with a density of 5.02%, contains about 18.8% and 63.3%, of TiO_2, and Fe_2O_3, respectively.

Table 2 Chemical composition and density of ilmenite and magnetite

Oxide	Ilmenite	Magnetite
Na_2O	0.2	0.30
MgO	1.41	0.80
Al_2O_3	1.3	2.60
SiO_2	3.37	8.17
P_2O_5	0.01	0.12
K_2O	0.2	0.30
CaO	2.15	2.12
TiO_2	42.8	18.8
MnO	0.85	0.40
Fe_2O_3	44.8	63.3
LOI	1.1	1.21
Density (g/cm^3)	4.64	5.02

3.2 Specific radiological activities

Table 3 shows the specific activity concentrations of the main naturally occurring radionuclides measured in the studied minerals.

Table 3 Specific activity concentrations of the main NORMs in zircon and magnetite

Mineral	$^{238}U(^{226}Ra)$, Bq/kg	^{232}Th, Bq/kg	^{40}K, Bq/kg
Ilmenite	33.3±3.25	35±1.5	112±4.7
Magnetite	22.2±2.1	25±1.2	91±4.5

The measured specific activities show a big difference between the zircon and magnetite. The measured specific activities of $^{238}U(^{226}Ra)$ in zircon and magnetite are; 2342±200, and 22.2±2.1 Bq/kg, and those of ^{232}Th are; 1757±70 and 25±1.2 Bq/kg. The obtained values are far away higher than the mean international activity concentrations in the soil as reported by the UNSECAR at 35 and 30 Bq/kg for ^{226}Ra and ^{232}Th, respectively, and 50 Bq/kg for ^{226}Ra and ^{232}Th in typical masonry [18, 20] for zircon and lower than the limits for magnetite. The blending of two minerals in a specific ratio may produce a heavy mixture with permissible activity concentration.

The specific activity of ^{40}K contained in both minerals is lower than the mean international value in soil, 400 Bq/kg [21-22].

3.3. Statistical Analysis

Table 4 shows the results of the statistical design of magnetite and ilmenite percentages and the effect of different mixture combinations on the mixture density and radioactive concentrations. Of course, the highest density is achieved when both magnetite and ilmenite were used. However, the highest density is not the only constraint where radioactivity comes into the picture. Therefore, the optimization of getting a mixture with the highest density and allowable radioactive concentration is a mandatory step. In addition, Tables 5-8 show the analysis of variance (ANOVA) tables for density and various radioactive nuclides. The statistical analyses show that the resulting models are significant with R-squared equals 0.9959, 0.9998, 0.9999, and 0.9999, and standard deviations are 0.072, 0.15, 0.1, and 0.25 for density, ^{226}Ra ^{232}Th, and ^{40}K, respectively. In addition, The ANOVA shows that the following factors A, B, and AB are significant model terms for variously studied responses. The significance of each factor is interchangeable according to the properties associated with that factor. For instance, the magnetite (factor A) is higher in density, thus, its effect is higher in getting a mixture with higher density. Similarly, the ilmenite is more significant in the determination of the radioactivity of the resulting mixture due to its higher radioactive content for various isotopes. Although the interaction between the factors (AB) is insignificant in the case of density and ^{40}K, it plays a significant role, especially in cases ^{226}Ra and ^{232}Th where it exceeds the effect of the main factor (A). The models can be used to estimate the design responses within the design space.

Furthermore, the curvature is only significant in the determination of radioactive concentrations.

Table 4 Statistical design results of different responses at various factors combinations

Std	Factor		Response			
	A	B	1	2	3	4
	Magnetite, %	Ilmenite, %	Density	^{226}Ra	^{232}Th	^{40}K
1	0	0	2.65	0	0	0
2	50	0	3.9	12	13	46
3	0	50	3.65	19.6	17.5	57
4	50	50	4.87	16	15	58
5	25	25	3.76	4	7.8	13.5
6	25	25	3.9	4.2	7.7	14
7	25	25	3.8	3.9	7.6	13.7

Table 5 Density ANOVA table of factorial model [Partial sum of squares]

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	2.5	3	0.83	159.98	0.0062	significant
A	*1.53*	1	*1.53*	*293.31*	*0.0034*	
B	*0.97*	1	*0.97*	*186.58*	*0.0053*	
AB	*2.250E-04*	1	*2.250E-04*	*0.043*	*0.8545*	
Curvature	4.725E-03	1	4.725E-03	0.91	0.4411	Not significant
Pure Error	0.010	2	5.200E-03			
Cor Total	2.51	6				

Table 6 ANOVA table of factorial model for 226Ra [Partial sum of squares]

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	217.72	3	72.57	3110.29	0.0003	significant
A	*17.64*	1	*17.64*	*756.00*	*0.0013*	
B	*139.24*	1	*139.24*	*5967.43*	*0.0002*	
AB	*60.84*	1	*60.84*	*2607.43*	*0.0004*	
Curvature	106.09	1	106.09	4546.61	0.0002	Significant
Pure Error	0.047	2	0.023			
Cor Total	323.85	6				

Table 7 ANOVA table of factorial model for 232Th [Partial sum of squares]

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	182.69	3	60.90	6089.58	0.0002	significant
A	*27.56*	1	*27.56*	*2756.25*	*0.0004*	
B	*95.06*	1	*95.06*	*9506.25*	*0.0001*	
AB	*60.06*	1	*60.06*	*6006.25*	*0.0002*	
Curvature	23.15	1	23.15	2315.25	0.0004	Significant
Pure Error	0.020	2	0.010			
Cor Total	205.86	6				

Table 8 ANOVA table of factorial model for 40K [Partial sum of squares]

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	2248.75	3	749.58	11835.53	< 0.0001	significant
A	*552.25*	1	*552.25*	*8719.74*	*0.0001*	
B	*1190.25*	1	*1190.25*	*18793.42*	*< 0.0001*	
AB	*506.25*	1	*506.25*	*7993.42*	*0.0001*	
Curvature	1205.37	1	1205.37	19032.19	< 0.0001	Significant
Pure Error	0.13	2	0.063			
Cor Total	3454.25	6				

The coefficient estimation within a 95% confidence interval for each factor and factors interactions in different produced models was generated by the software. The generated models either coded or as actual factors are given in the equations 1-4 and 5-8, respectively.

Final Equation in Terms of Coded Factors:

Density =+3.77+0.62 * A+0.49 * B-7.500E-03 * A * B

^{226}Ra =+11.90+2.10 * A+5.90 * B-3.90 * A * B

^{232}Th =+11.38+2.62 * A+4.87 * B-3.87 * A * B

40K =+40.25+11.75 * A+17.25 * B-11.25 * A * B

Final Equation in Terms of Actual Factors:

Density =+2.65+ 0.025 * A + 0.02 * B - 1.2E-05 * A * B

226Ra, Bq/kg = -3.357E-015+0.24 * A+0.392 * B - 6.24E-03 * A * B

232Th, Bq/kg =-7.72110E-015+0.26 *A+0.35*B-6.2E-03 * A * B

40K, Bq/kg = -1.61136E-014+0.92 * A +1.14000* B-0.018 * A * B.

Where,

A: Magnetite, %

B: ilmenite, %

3.3.1. Contour plots

Figures 1-4 show the contour plot of the different responses as a function of the studied factors (i.e., magnetite % and ilmenite %). Figure 1 shows that the higher the magnetite and ilmenite in the mixture the higher the density. In terms of the radiological activity concentrations, all the isotope concentrations increase with increasing the ilmenite %. The presence of the magnetite lowers the radioactive concentrations in Figures 2-4.

Figure 1 Density as a function of magnetite and ilmenite percentages

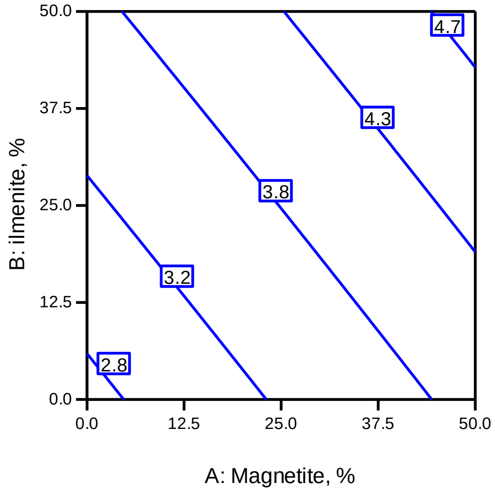


Figure 2 Effect of magnetite and ilmenite content on 226Ra-specific activity concentration

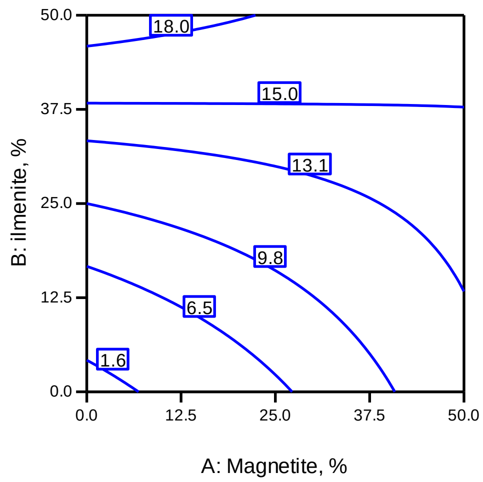


Figure 3 Effect of magnetite and ilmenite content on ^{232}Th specific activity concentration

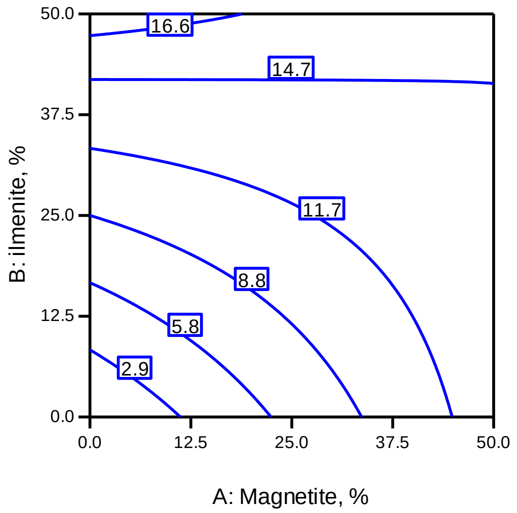
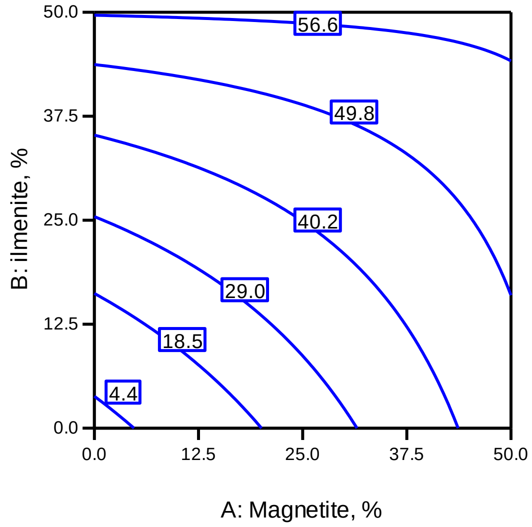


Figure 4 Effect of magnetite and ilmenite content on ^{40}K specific activity concentration



3.3.2. Optimization

To achieve a mixture with the highest density and permissible radioactivity limits the optimization tool was used to get the possible solutions. Table 9 shows the input data and constraints for the optimization process. Running optimization, with 100 cycles per optimization produces 8 possible solutions, with desirability between 0.9-1.0, which represents the possible mixture that maximizes the density of the mixture with radioactive concentrations within the standard allowable limits, Table 10.

Table 9 Optimization data and constraints

Constraints	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
Magnetite, %	**in range**	0	50	1	1	3
ilmenite, %	**in range**	0	50	1	1	3
Density	**maximize**	2.65	4.87	1	1	3
226Ra, Bq/kg	**in range**	0	30	1	1	3
232Th, Bq/kg	**in range**	0	30	1	1	3
40K, Bq/kg	**in range**	0	400	1	1	3

Table 10 The suggested possible solutions generated by optimization

Solution No.	Magnetite, %	ilmenite, %	Density	^{226}Ra	^{232}Th	^{40}K	Desirability
1	50	50	4.87	16	15	58	1.0
2	50	49.73	4.865	16	15	58	0.998
3	50	49.05	4.852	16	15	58	0.992
4	49.03	50	4.85	16	15	58	0.989
5	46.17	50	4.78	16	15	58	0.958
6	45.64	50	4.76	16	15	58	0.952
7	45.08	50	4.75	16	15	58	0.946
8	44.17	50	4.73	16	15	58	0.936

Conclusions

The statistical design of the experiment was used to find an optimum solution for producing the best mixture by blending magnetite and ilmenite. The importance of each mineralogical component (magnetite and ilmenite) on the studied responses; namely density, and radioactive concentrations (i.e., ^{226}Ra, ^{232}Th, and ^{40}K) was indicated using factorial design. The statistical analysis by F-test and analysis of variance indicated the significance of magnetite amount for increasing the density of the mixture while the ilmenite content is very effective in controlling the radioactive concentration where the higher the ilmenite content is the higher the radioactive measures. Finally, using the optimization tool produces eight possible solutions that represent a mixture with a density as high as 4.73-4.87 with radioactive concentration measures as low as 16, 15, and 58 Bq/kg for ^{226}Ra, ^{232}Th, and ^{40}K, respectively.

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