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Radio Activity Associated with Gypsum Leaching Process during the Production of Common Salt

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ABSTRACT

The dissolution pattern of alpha and beta activity from gypsum sample when leached with 50,100,150ml of rain water,at different time intervals was determined. The dissolution rate increases if the solid to liquid ratio(gypsum to rain water volume) increases.It also increases with time , even though faster in the initial stages, slower in the subsequent stages. The dissolution rates are also influenced by the acidity, alkalinity, and chemical property of the leaching medium. The salinity also has its effect on leaching pattern. The gypsum which contains radio activity due to $^{226+228}$Ra was determined.

Key words: Alpha, Beta, Leaching, Radio activity.

INTRODUCTION

Natural radio activity arises mainly from primordial radio nuclides, such as ^{40}K and the isotopes in the ^{238}U,^{235}U and ^{232}Th decay series which are present in at least trace amounts in all ground formation[1].Naturai environmental radio activity and the associated external exposure due to gamma radiation depend primarily on geological and geographical conditions and appear in different amounts in each region of the world[2,3,4].A significant part of the total dose from of natural sources comes from terrestrial gamma emitting radio nuclides[5].Indoor radiation exposures are mainly due to radon ^{222}Rn,Thoron(^{220}Rn) and their daughters[6]. Gypsum is a very soft mineral composed of calcium sulphate dihydrate, with the chemical formula $CaSO_4 \cdot 2H_2O$[7]. The phase chemistry of solar salt production is conveniently divided into four distinct phases[8]. The second phase extending from 13 to 25.4°Be centres around gypsum, $CaSO_4.2H_2O$, which crystallizes as needle shaped crystals from 13 to 16.4°Be. Gypsum contains elevated levels of impurities, as a result they are dumped or stock piled near to the production site. Among the impurities present in gypsum are soluble in water and may dissolve in rain water and through this to ground water or pond water. Very few studies have addressed the mobility of radium from gypsum. The reports showed that radium is leachable in water

from calcium carbonate fertilizer process waste[9].The earlier study showed that the natural gypsum and gypsum derived products have traces of radio activity. The hazard indices were lower than the acceptable limit(1) recommended for building materials. However, the associated levels are not detrimental to health[10].Another study reports, the natural radio activity levels are associated with either natural gypsum or gypsum from flue gas desulphurization units, and low exhalation rates with other products like clay bricks[11]. A study showed that the gypsum used as building materials in Turkey, do not pose any excess radiological health problem and are safe for use in the construction of buildings[12]. Gypsum produced from the process of production of common salt at Vepalodai, Tuticorin district was taken for the present study.

MATERIAL AND METHODS

About 500g of gypsum from Vepalodai salt work, Tuticorin district (Plate-1) is utilized for the experiments. The initial α and β activity of gypsum is estimated at 2.802Bqg^{-1} and 4.863Bqg^{-1} respectively. Leaching experiments were performed in the laboratory using rain water as leachant. Estimation of radio activity in gypsum using multichannel analyzer.Gypsum samples were leached with water under the following conditions;

Batch wise leaching with rain water

Ten gram of gypsum sample was placed in a two litre beaker, one litre of rain water having pH of 7.30 was added, stirred for one minute and kept for various time intervals varying from 0 to 2160 hours. The leachate was then collected, and α and β activity of gypsum was counted. The experiment was repeated several times by changing the contact time.

Leaching of ^{226}Ra with varying liquid solid ratio

A leaching study was conducted with different liquid solid ratios (V/M), using rain water with a pH of 7.30 as the leachant. For this experiment a constant weight of 10g each of gypsum sample having an initial α and β activity 2.802Bqg^{-1}and 4.863 Bq/g respectively was used. Approximately ten grams of gypsum was collected in three beakers and 50,100,150 ml of rain water was added to each beaker having gypsum sample. The mixture was stirred for one minute using a glass rod and was allowed to settle for half an hour. The supernatant liquid was removed and ^{226}Ra analysis was carried out by counting gross alpha and gross beta activity. The experiments were repeated.

Leaching of ^{226} Ra with different contact time

Without disturbing the above experimental arrangements, the contact time with leachant and leachate was varied. The contact time is varied from 1hour to 3 months. At each time the leachate and leachant were analyzed for α and β activity. The results were tabulated with the activity at various time intervals were fitted in a linear regression of the form Y = AX + B and the parameters of fitting A, B and R were calculated (α and β separately). This gives the leaching tendency of ^{226}Ra in gypsum (from Vepalodai salt work, Tuticorin District) under experimental conditions.

RESULTS AND DISCUSSION

Dissolution of gypsum using 50,100,150ml of rain water (alpha activity)

Table1 gives the dissolution pattern of μ activity from the gypsum sample, when leached with 50,100,150 ml of rain water, at different time intervals.When leached with 50ml of rain water the initial activity of the sample was normalised to 2.802 Bqg^{-1}. After one hour of contact time, the activity reduced to 1.426 Bqg^{-1} and after two hours it reduced to 1.008 Bqg^{-1}. The sample was leached for a maximum period of 2160 hours. The activity ended up with 0.099 Bqg^{-1}. When leached with 100 ml of rain water, at different time intervals, the initial activity of the sample was normalised to 2.802 Bqg^{-1}. After one hour of contact time, the activity reduced to 1.428 Bqg^{-1} and after two hours it reduced to 1.226 Bqg^{-1}. The sample was leached for a maximum period of 2160 hours. The activity ended up with 1.11 Bqg^{-1} .When leached with 150 ml of rain water, at different time intervals, the interval activity of the sample was normalised to 2.802 Bqg^{-1}. After one hour of contact time, the activity reduced to 1.321 Bqg^{-1} and after two hours it reduced to 1.485 Bqg^{-1}. The sample was leached for a maximum period of 2160 hours. The activity ended up with 0.654 Bqg^{-1}. It can be seen that the activity reduces or leach at a faster rate initially. This may be due to the presence of loosely bound activity, with the sample.

Table 1: Dissolution of gypsum using 50, 100, 150 ml of rain water (α activity)

Time (hours)	50ml of rain water (alpha activity)		100ml of rain water (alpha activity)		150ml of rain water (alpha activity)	
	Observed Activity (Bqg^{-1})	Estimated Activity (Bqg^{-1})	Observed Activity (Bqg^{-1})	Estimated Activity (Bqg^{-1})	Observed Activity (Bqg^{-1})	Estimated Activity (Bqg^{-1})
0	2.802	2.802	2.802	2.802	2.802	2.802
1	1.426	1.237	1.428	1.782	1.321	1.756
2	1.008	1.128	1.226	1.776	1.485	1.752
3	-	1.111	1.521	1.621	1.468	1.748
4	1.09	1.07	-	1.58	1.541	1.647
5	-	0.431	1.321	1.47	-	1.621
24	0.301	0.326	1.32	1.35	1.321	1.501
360	0.184	0.195	1.18	1.35	1.421	1.46
720	0.152	0.169	1.14	1.26	1.312	1.356
1440	0.129	0.123	1.12	1.12	1.121	1.237
2160	0.099	0.101	1.98	1.07	0.654	0.653

A = 1.24	A = 1.78	A = 1.756
B = -2.3×10^{-4}	B = -2.1×10^{-4}	B = -6.2×10^{-4}
R = -0.85	R = -0.93	R = -0.91

Table 2: Dissolution of gypsum using 50, 100, 150 ml of rain water (β activity)

Time (hours)	50ml of rain water (alpha activity)		100ml of rain water (alpha activity)		150ml of rain water (alpha activity)	
	Observed Activity (Bqg^{-1})	Estimated Activity (Bqg^{-1})	Observed Activity (Bqg^{-1})	Estimated Activity (Bqg^{-1})	Observed Activity (Bqg^{-1})	Estimated Activity (Bqg^{-1})
0	4.863	4.921	4.863	4.863	4.863	4.863
1	4.162	4.714	3.118	3.572	4.118	4.278
2	2.112	2.835	3.021	3.563	3.002	3.128
3	-	2.653	-	3.455	2.847	3.116
4	-	2.163	1.947	2.823	-	2.822
5	1.628	1.982	-	2.273	-	2.487
24	1.522	1.724	2.001	2.116	1.489	2.175
360	1.534	1.564	1.567	1.765	1.998	1.982
720	0.684	0.788	0.742	0.792	1.462	1.145
1440	0.701	0.768	0.624	0.754	0.147	0.195
2160	0.184	0.194	0.589	0.587	0.187	0.185

A = 4.863	A = 3.57	A =4.278
B = -1.56×10^{-3}	B = -1.38×10^{-3}	B = -6.8x10-3
R = -0.78	R = -0.72	R= -0.69

Afterwards, the leaching rate reduces and towards the end to it appears that the dissolution is very slow. The apparently different rate of leaching also can be attributed to the different pattern and distribution of activity at various layers of the matrices, which is often referred as the onion ring assembly.

The observed activity at various time intervals was fitted in an equation of the form At = Ao $e^{-\lambda t}$, where At is the activity at time (t = 0 to 2160 hours), Ao is the initial activity, λ is the decay constant. These values were used to estimate the more probable activity using least square technique and the estimated activity thus obtained at various time intervals was derived. The table1 gives the A, B and R values, the parameters of fitting. The correlation coefficient for the first sample shows to be 0.85, second sample shows to be 0.93, third sample shows to be 0.91, it indicates reasonably good fitting.

Dissolution of gypsum using 50,100,150ml of rain water (beta activity)

Table 2 gives the dissolution pattern of b activity from the gypsum sample, when leached with 50,100,150 ml of rain water, at different time intervals. When leached with 50ml of rain water, the initial activity of the sample was normalised to 4.863 Bqg^{-1}. After one hour of contact time, the activity reduced to 4.162 Bqg^{-1} and after two hours it reduced to 2.112 Bqg^{-1}. The sample was leached for a maximum period of 2160 hours. The activity ended up with 0.184 Bqg^{-1}. When leached with 100 ml of rain water, the initial activity of the sample was normalised to 4.863Bqg^{-1}. After one hour of contact time, the activity was reduced to 3.118 Bqg^{-1} and after two hours it reduced to 3.021 Bqg^{-1}. The sample was leached for a maximum period of 2160 hours. The activity ended up with 0.589 Bqg^{-1}. When leached with 150ml of rain water, the initial activity of the sample was normalized to 4.863 Bqg^{-1}. After one hour of contact time,the activity was reduced to 4.118Bqg^{-1} and after two hours it reduced to 3.002Bqg^{-1}. The activity ended up with 0.187 Bqg^{-1}. Here also the activity of leaching is very fast in the initial stage, subsequently the leaching rate is reduced and the dissolution is very slow, for reasons as discussed previously. Table 2 also gives the parameters of fitting A,B and R. The correlation coefficient for the first sample shows to be 0.78, second sample shows to be 0.72 ,third sample shows to be 0.69 it indicates reasonably good fitting.

The negative sign of correlation coefficient indicates negative correlation as the activity decreases with increasing time of contact. The dissolution rate here is influenced by the solid to liquid ratio. If the solid to liquid ratio increases the dissolution rate also goes up.

As a general observation it can be noted that there is an initial fast rate of dissolution of the gypsum sample. Subsequently the leaching rate is reduced, due to several factors associated with the bonding of ^{226}Ra and $CaSO_4.2H_2O$ (Gypsum). Also peculiar dissolution pattern observed in some cases indicates the distribution pattern of ^{226}Ra in different layers of gypsum, which is generally referred as 'Onion ring assembly'.

Another observation of the study is that the dissolution rate increases if the solid to liquid ratio (gypsum to rain water volume) increases. It also increases with time, even though faster in the initial stages, slower in the subsequent stages. The dissolution rates are also influenced by the acidity, alkalinity, and chemical property of the leaching medium. The salinity also has its effect on leaching pattern.

CONCLUSION

The present study assumes importance because of the use of gypsum in several industrial and household activities. The gypsum which contains radioactivity due to $^{226+228}Ra$ is something important to monitor and assess, as huge quantity of gypsum is heaped at various parts of the country. The rainwater washes this activity to the nearby soil and drinking water sources and thereby providing additional external and internal radiation dose to the general public and residents of the local area. As radioactivity is harmful to human life, a clear cut method of handling and disposal of the same is required. The study gives valuable information for the regulatory aspects.

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