GO follows free radical mechanism and shows features (increase in concentration, elimination of water) that are similar to thermal reduction.

In summary, our results show that graphite oxide prepared by Hummer's method is EPR-active. Thermal treatement leads to co-elimination of CO_2 and H_2O and a large enhancement in transient free radicals, finally leading to EPR-inactive graphitic material. It appears possible that single sheets of GO deposited on mica substrates may be thermally converted to graphene-like molecule. However, significant loss of carbon occurs in the thermal process and therefore the path towards pure graphene via Hummer's GO is less attractive.

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ACKNOWLEDGEMENT. We thank Prof. S. Ramakrishnan, IPC Department, Indian Institute of Science, Bangalore, for TG-MS data.

Received 15 September 2008; revised accepted 7 July 2009

Radioactivity associated with common salt and estimation of ingestion dose to the general public

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The sea brine and sub-soil brine used for the manufacture of common salt contain several chemical and radioactive elements. This study estimated the gross alpha and gross beta activities from the sea and sub-soil brine at two salt works at Kovalam and Puthalam in Kanyakumari District, Tamil Nadu. The activity of the sea brine was higher than that of the sub-soil brine. The gross activity was increasing at subsequent stages of production due to the concentration of brine. The sediments and gypsum samples collected at different stages were also subjected for estimation of different types of activity. ^{40}K activity was found to increase, source to bittern, from 8.6 to 162.16 Bq l^{-1} at Kovalam and 8.59 to 198.98 Bq l^{-1} at Puthalam. The ingestion dose due to consumption of salt was calculated to be 13.61 μSv per year, the highest contribution (12.42 μSv) coming from $^{226+228}$Ra. This study shows the influence of natural high-background radiation areas on the radioactivity in common salt and calls for setting limits for radioactivity contents in it.

Keywords: Alpha–beta activity, gypsum, salt works, sea and sub-soil brine, sediments.

COMMON salt (NaCl) has several applications in the chemical industry, which consumes 94% of the salt produced, and the rest (6%) is consumed by the human population[1]. Manufacture of common salt from sea water or natural brine using solar energy and wind is a popular process. The brine is pumped to large reservoirs of 3–4 m depth and made to flow through underground trenches to a distance of 3 km and stored there. This brine is sent to primary, secondary and tertiary condensers, arranged in series, for evaporation. The concentrated brine from condensers is let into crystallizers, for production of salt, using solar energy[2]. The original volume of the water reduces to 3%, when bittern (the supernatant liquid obtained after the precipitation of NaCl) is formed[3]. The brine density expressed as salinity Baume (°Be), is a

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good leaching agent of radioactivity. This aspect also requires some examination due to proximity of the salt pans to natural high-background areas. Further, at a salinity of 13–24°Be, $CaSO_4 \cdot 2H_2O$ (gypsum) gets precipitated at the condenser stage[4]. Because of the chemical affinity, Ra, Th, etc. are also susceptible to precipitation and subsequent removal. This advantageously eliminates radioactivity from the common salt, without the addition of any external agents. Potassium, another natural radionuclide of immense importance in the body functions and metabolism, is an important constituent of sea water (~1 g/l), and likely to follow a different pattern from the brine to bittern stage, due to its high solubility. It is estimated that the human receives about 0.20 m Gy/y of radiation dose due to ^{40}K present in our body[5]. Bittern, reported to have secondary nutrients like Mg, Ca, K and sulphates is being used for the magnesium demanding horticulture crops[6].

The present study has been carried out on common salt manufactured from two salt works at Kanyakumari District of Tamil Nadu. Whereas Kovalam salt work uses the sea brine from Arabian sea, Puthalam salt work uses the sub-soil brine. As Kovalam salt work locates around the natural high background radiation areas of Kanyakumari District, the influence of this area on radioactivity concentrations in the common salt is of interest. As potassium along with sodium has several vital functions in the metabolism and electrolyte balance of human body, the concentration of potassium in NaCl is also examined. Ionizing radiation, in general, emanating from the natural high-background areas of the globe, has invited the attention of the scientific community[7]. The study estimates radioactivity associated with gypsum and the supernatant water samples, before and after the production of salt. This communication discusses statistical analysis of the results and minimum detectable levels of different activity. The likely ingestion dose received by the general public due to the consumption of common salt is also worked out.

Brine, sediments, bittern and salt formed at different stages of manufacture of common salt, were collected on a monthly basis for one year, May 2006 to April 2007. The radioactivity of the brine samples was calculated after the precipitation by $BaCl_2$ and $CaSO_4$. The composite samples were dried in an electrical air oven at 120°C, powdered in an agate mortar and suitable amount of substances were counted for α and β activity. Gross alpha and gross beta activities were determined using low-background alpha counting system ZnS (Ag), ECIL, Model RCS-4027, and gas flow beta counting system (ECIL Model BCS 36A). The efficiency of the alpha counter was determined using ^{239}Pu source of strength 542 dpm (disintegration per minute) and the efficiency was estimated to be 30%. KCl with beta activity of 1000 Bq was used for estimating beta efficiency, which was calculated to be 40%. For the estimation of gamma efficiency, pure monazite sources of known strengths were used and the daughter products such as ^{208}Tl, ^{228}Ac, ^{214}Bi were considered assuming equilibrium with the parents. This assumption generally holds good as the minerals do not undergo any chemical processing. The comparison of different peaks also gives an idea of equilibrium. Th and U activity in the common salt were determined by counting 500 g of samples in MCA, with 2″ × 2″ NaI (Tl) as detector[8]. ^{208}Tl (2614 KeV, 100% emission) and ^{214}Bi (609 KeV, 46% emission) peaks were taken for calculation of Th and U respectively, assuming equilibrium. ^{228}Ac (910 KeV, 29%) represents ^{228}Ra and the peak energy of 1460 KeV (11%) was considered for ^{40}K. The counting time varied from 5000 to 10,000 s for maximum accuracy possible.

When radioactivity, particularly of low levels is measured, it is essential to make an assessment on the accuracy of the result in terms of percentage error and confidence level. Hence, the result presented in this work has also undergone such an analysis. From a series of studies done on calibration and derivation of the sensitivity of the system, it has been concluded that the system has a background of 0.340, 0.212, 0.101 and 0.097 cps for ^{208}Tl, ^{214}Bi, ^{40}K and ^{228}Ac respectively. With mineral monazite and KCl as standard sources, the derived sensitivities for different energies of interest were calculated to be 8.78×10^{-4}, 7.6×10^{-3}, 1.46×10^{-3} and 4.5×10^{-3} cps Bq^{-1} for ^{208}Tl, ^{214}Bi, ^{40}K and ^{228}Ac respectively. Thus for ^{208}Tl, with the highest background and lowest sensitivity, a background of 0.34 cps works out to 380 Bq. It is quite imperative that the estimation of low level of activity involves a lot of uncertainty. Hence, the lowest activity that can be presented with relatively low error and better confidence level has been calculated based on the relation,

$$\sigma = \sqrt{\frac{r_g}{t_g} + \frac{r_{bg}}{r_{bg}} \times \frac{1}{(r_g - r_{bg})}},$$

where r_g is the counting rate of the sample, t_g the counting time in seconds, r_{bg} the background counting rate and

Table 1. Mean and standard deviation values of radioactivity associated with brine samples at various stages of production of salt

Salt works	Various stages	Activity (Bq l^{-1}) Gross α	Gross β
Kovalam (sea brine)	Source	0.001 ± 0.00009	0.0291 ± 0.001
	Reservoir	0.0022 ± 0.0001	0.0352 ± 0.002
	Condenser	0.0029 ± 0.0001	0.0405 ± 0.002
	Crystallizer	0.0033 ± 0.0002	0.0441 ± 0.002
	Bittern	0.004 ± 0.0002	4.4930 ± 0.224
Puthalam (sub-soil brine)	Source	BDL	0.0194 ± 0.001
	Reservoir	0.0010 ± 0.00005	0.0291 ± 0.001
	Condenser	0.0015 ± 0.00008	0.0308 ± 0.002
	Crystallizer	0.0020 ± 0.0002	0.0340 ± 0.002
	Bittern	0.0031 ± 0.0001	3.2352 ± 0.162

Table 2. Mean and standard deviation values of radioactivity associated with the sediments collected at various stages of production of salt

		Activity (Bq kg^{-1})			
Salt works	Various stages	Gross α	Gross β	^{208}Tl	^{228}Ac
Kovalam (sea brine)	Source	44.0 ± 1.2	2005.0 ± 99.25	164.4 ± 17.00	59.8 ± 6.01
	Reservoir	97.0 ± 4.85	653.0 ± 32.65	73.3 ± 7.33	34.1 ± 3.22
	Condenser	158.0 ± 6.92	3032.0 ± 150.16	169.9 ± 18.01	172.5 ± 17.52
	Crystallizer	190.0 ± 9.50	1930.0 ± 95.50	137.7 ± 11.20	69.5 ± 6.89
	Bittern	383.0 ± 20.15	2683.0 ± 130.15	126.1 ± 12.52	93.1 ± 9.22
Puthalam (sub-soil brine)	Source	14.0 ± 0.71	1637.0 ± 81.85	210.8 ± 21.00	65.2 ± 6.52
	Reservoir	38.0 ± 2.00	723.8 ± 35.15	98.4 ± 8.92	33.0 ± 3.25
	Condenser	62.0 ± 3.12	1981.2± 100.05	195.7 ± 20.01	71.7 ± 7.50
	Crystallizer	95.2 ± 3.42	1190.0 ± 59.51	187.5 ± 17.65	69.2 ± 7.01
	Bittern	107.3 ± 5.35	1372.0 ± 65.86	167.2 ± 17.01	49.5 ± 5.02

Table 3. Mean and standard deviation values of the radioactivity associated with the concentration of ^{40}K in brine at various stages of salt production

Salt works	Stages	^{40}K activity (Bq l^{-1})
Kovalam (sea brine)	Source	8.60 ± 0.92
	Reservoir	12.45 ± 1.26
	Condenser	18.38 ± 1.73
	Crystallizer	68.18 ± 6.82
	Bittern	162.16 ± 15.94
Puthalam (sub-soil brine)	Source	8.59 ± 0.92
	Reservoir	21.45 ± 2.10
	Condenser	27.27 ± 2.27
	Crystallizer	88.93 ± 9.21
	Bittern	198.98 ± 18.91

t_{bg} is the background counting time. It has been calculated that an activity of 10 Bq can be presented with 10% error at 1σ, if the sample is counted for 8078 s. Hence, all the samples were counted for a rounded up period of 8000 s. For other radionuclides, because of their better sensitivity and comparatively lower background, still lower values can be presented with better reliability.

With a system background of 2 counts per 5000 s and an efficiency of 30%, α activity of 0.001 Bq is presented with 5% error at 2σ. Similarly, β activity is also presented with 5% error at 2σ, as they are counted for 3000 s, in a low background (3 counts per min) beta counting system having high efficiency (40%; ref. 9). The MDL for gamma activity can be stated to be 10 Bq/kg with 10% error at 1σ.

Table 1 provides the details of radioactivity encountered at various stages of the production of salt from two sources at Kovalam and Puthalam. Gross α and gross β activities are minimum at the brine stage. The activity gets increased as the brine concentrated in the subsequent stages. At bittern stage, there is a drastic increase in the beta activity, disproportional to the earlier pattern. Subsequent analysis of the brine samples revealed the accumulation of ^{40}K in the bittern, as potassium salt is highly soluble and remains mostly with the solution, while the salt gets crystallized. This trend also indicates that radioactivity originating from Th and U preferred to stay with solid samples. The gamma-ray activity was directly related to abundance of the primordial radionuclides in the area[10]. The samples of Kovalam showed higher activity than those of Puthalam at all stages, indicating that the surface brine sample is more active than the sub-soil brine. The influence of natural high-background radiation areas on the Kovalam samples is also evident.

Table 2 gives the radioactivity associated with the sediments collected at different stages of production of salt at Kovalam and Puthalam. The sediments collected at the condenser stage showed maximum beta activity and can be attributed to the precipitation of gypsum, at this stage, at salinity above 19°Be. Gypsum ($CaSO_4 \cdot 2H_2O$) carries similar radioactive substances like Ra, Th, etc. along with it, resulting in higher radioactivity. Here again the samples from Kovalam showed activity higher than that of Puthalam, as observed in Table 1, indicating a lower activity for sub-soil brine than that of surface brine. ^{208}Tl and ^{228}Ac normally used for representing Th activity in gamma spectrometric analyses. But here, it can be seen that there is clear disequilibrium between these two radionuclides. This also indicates that $^{226,228}Ra$ has separate sources of origin, other than Th and U. The higher activity of ^{228}Ac at the condenser stage is an indication of higher precipitation of ^{228}Ra at this stage, due to high salinity.

Table 3 provides the concentration of ^{40}K with the brine at various stages of production. There is a steady increase of potassium activity in the brine at various stages, as its concentration gets increased, the highest being at the bittern stage. The original volume of the brine is reduced to 3% at bittern stage. This trend also indicates the high solubility of potassium salts.

Table 4 gives the distribution of activity in gypsum collected from Kovalam and Puthalam. The predo-

Table 4. The mean and standard deviation values of radioactivity of gypsum sample formed at the condensers

	Radioactivity (Bq kg^{-1})				
Salt works	Gross α	Gross β	^{208}Tl	^{228}Ac	^{214}Bi
Kovalam (sea brine)	298 ± 14.25	5323 ± 265.30	202 ± 21.00	2242 ± 210.55	128 ± 12.92
Puthalam (sub-soil brine)	126 ± 8.01	2220 ± 111.0	110 ± 12.20	1873 ± 180.37	101 ± 11.51

Table 5. The mean and standard deviation values of radioactivity in common salt

	Radioactivity (Bq kg^{-1})				
Salt works	Gross α	Gross β	^{208}Tl	^{228}Ac	^{214}Bi
Kovalam (sea brine)	31.7 ± 1.78	110.0 ± 6.50	10.6 ± 1.35	14.40 ± 1.54	11.20 ± 1.12
Puthalam (sub-soil brine)	10.3 ± 0.62	30.60 ± 1.83	8.26 ± 8.21	11.02 ± 1.21	4.6 ± 0.54

Table 6. Estimation of ingestion dose to the general public due to the annual consumption of (2 kg) common salt[11]

	Contributions from 2 kg salt		
Specification	^{232}Th	$^{226+228}$Ra	^{238}U
Av. concentration (Bq)	26.66	36.02	26.70
Dose coefficient (Sv Bq^{-1})	2.3×10^{-7}	6.9×10^{-7}	4.5×10^{-8}
Ingestion dose (μSv y^{-1})	0.58	12.43	0.60

minance of ^{228}Ac in the gypsum sample shows the overwhelming presence of ^{228}Ra in the sample due to its chemical affinity with Ca. The ratio of gross α and gross β activities normally observed in Th and U sources, gets distorted in the present case. This can be attributed to the presence of other beta emitters, mainly radium originating from radio ferrous rocks. ^{208}Tl and ^{214}Bi activity, which can be representative of Th and U, indicates nearly equal presence in the gypsum. An analysis of the gross β and ^{228}Ac activity indicates the presence of ^{226}Ra also.

Table 5 shows the analysis of radioactivity in the salt product. The radioactivity in the salt produced from the sea brine is higher than that of sub-soil brine. This is true in the case of ^{208}Tl, ^{228}Ac and ^{214}Bi. As the ^{208}Tl activity is not matching with ^{228}Ac activity, it can be concluded that disequilibrium exists between Th and Ra in all the cases. Hence ^{208}Tl activity can be considered that due to ^{232}Th and ^{228}Ac can be representative of ^{228}Ra, ^{214}Bi can be assumed to be due to ^{238}U. The salt sample produced from Puthalam sub-soil brine has gamma activity lower than that of Kovalam salt work.

Basic Safety Series (BSS 115, IAEA) published the estimated ingestion dose to general public and radiation workers due to ingestion of various radionuclides. These values have been adopted for the estimation of ingestion dose to the general public. An average man requires about 5 g of NaCl per day, but generally consumes slightly more. Assuming a consumption of 5 g per day, the aggregate consumption per year works out to about 2 kg. From Table 6, it can be seen that the annual intake of Th, Ra and U is 26.66, 36.02 and 26.7 Bq respectively. With the corresponding ingestion coefficients for the above radionuclides, the total ingestion dose works out to be 13.61 μSv per year. The highest contribution (12.43 μSv) coming from ^{228}Ra. This study calls for limits for radioactivity contents in common salt.

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Received 25 November 2008; revised accepted 25 June 2009