Impact of Hub Valley Groundwater on Scaling and Corrosion

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Abstract: Underground water sample from the wells of Hub Valley were analysed for their physio-chemical and thermodynamic parameters to study their corrosion / scaling trend. The positive values of Langelier Saturation Index (L.S.I.) show that 90% samples are scaling, whereas, the values of Ryznar Stability Index (R.S.I.) of 95% samples that are below 7, that the most of the samples are scalingand are not corrosive. Moreover the negative values of free energy change (ΔG) of underground water of Hub Valley also indicate that the 90% samples are scale forming. Sample No.9 is moderately corrosive and sample No.1 is low corrosive. The water can safely be used in cooling, heating and steam generating systems after simple treatment with acids, antiscalent, water softeners etc.

Key Words: Corrosion, Scaling, Underground water.

INTRODUCTION

The shortage of water in Karachi, due to rapid increase in population and industrial activity, has forced the people to meet their requirement from underground sources. Well water from Hub Valley is being supplied by tankers to various industries in Lesbela Industrial Area. Physico-chemical nature of the underground water of Korangi / Landhi was studied by Mahmood [1] and the water irrigation chemistry of the underground water in Hub Valley was studied by Qaimkhani [2]. Industry uses water as an ingredient in a finished product, as a buoyant transporting medium, as a cleaning agent, as a coolant and as a source of steam for heating and power production. The water quality requirements, for industrial processes vary greatly with the type of industry and function of the water. It is therefore not possible to set a single standard of quality for water used for varied industrial purposes. However the common industrial use of water is in cooling, heating and steam generation. The two most frequently encountered water problems in these systems are scale formation and corrosion. Corrosion / Scaling Trend of water of lower Jehelum canal was studied by Khan [3] and comparison of corrosion / scaling behaviour of water samples of Islamabad sartorial and National Park area was studied by Ahmed [4]. Minimising scale formation in pump system have been studied by DeGiorgio [5]. Langeliers Saturation Index (L.S.I) [6], is a very useful tool for the predication of corrosion / scaling behaviour of water on the metal surface. The L.S.I is applicable in the pH range of 6.5 to 9.5, Hammer [7]. Many natural waters contain soluble calcium and magnesium bicarbonates. By the addition of lime, calcium carbonate is precipitated on metal surface at an appropriate pH. The Langeliers Saturation Index (L.S.I) with respect to $CaCO_3$ is equal to the difference between the actual measured pH of a water and pH_S at saturation with $CaCO_3$.

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$$L.S.I. = pH - pH_S \quad (1)$$

$$pHs = pCa^{+2} + pAlk + C' \quad (2)$$

Where:- pCa^{+2} = –ve log of the calcium ion concentration in mole/litre

pAlk = –ve log of the total alkalinity, in equivalents/litre

C' = pKa – pKs = constant based on ionic strength & temp.

Where:- pka = Ionisation constant of HCO_3^{-1}

pks = Solubility product of $CaCO_3$

The rate of saturation with respect to calcium carbonate depends on the value of the Langelier Index as mentioned below [8]:

Salutation	Comments	Characteristic of water
+ ve	Over saturated with respect to $CaCo_3$	Protective film of $CaCO_3$
Zero	in equilibrium	Corrosive & can dissolve $CaCO_3$
– ve	Unsaturated with respect to $CaCO_3$	

Scale of LSI Hammer [7].

L.S.I.	EFFECT
> + 2.0	High scaling
+2.0 to +0.1	Moderating scaling
+0.1 to 0.0	Low scaling
0.0 to - 0.1	Low corrosive
-0.1 to –2.0	Moderating corrosive
< - 2.0	High corrosive

Another index, called Ryznar Stability Index (R.S.I) was proposed by Ryznar [9] using the empirical expression.

Rynar Stability Index = 2pHs – pH 3

R.S.I. < 7 Indicate a scale forming water

R.S.I. > 7 Indicate a corrosive water

This index is of particular interest in evaluating waters of widely different composition, but in any one plant if the saturation index and stability index are plotted daily on the same scale, one plot is simply the inverse of the other and has the same significance. The stability index does seem to have a particular value in predicting the performance of water when heated in hot-water heaters and coils.

The free energy (ΔG) change is a function of the solution alkalinity, calcium hardness and pH. As studied by Montgomery [10]. The ΔG can influence the rate of the scaling precipitation. Positive ΔG shows corrosion is expected whereas negative ΔG predicts scale formation.

$$\Delta G = -(0.0045701) \times (\text{Temp } °C+273) \times (L.S.I) \quad 4$$

EXPERIMENT

Water samples from 20 wells were collected in thoroughly washed plastic containers for this study. The most representative sample of the area was choosen to obtain better result. Analytical grade (A.R) chemicals were used in the preparation of reagents. Physical and chemical analyses were carried out in triplicate for each sample and the average values were recorded. The pH value was measured immediately after collection of samples using a portable digital pH meter and all other estimations were completed within two days after sampling, SO_4^{-2} and TDS were determined by gravimetric methods, Cl^- by argentometric method. Ca^{+2} and Mg^{+2} were determined by EDTA titration method and Na^+ and K^+ were determined by flame photometer [1].

RESULTS AND DISCUSSION

Water samples from the wells of Hub Valley were collected and analysed for their physico-chemical constituents. The results are tabulated in Table **1**. Corrosion and scaling behaviour of the water samples were studied by analysing their thermodynamic parameters. The results are tabulated in Table **2**.

The pH values were in the range of 6.59 to 8.26. This shows that langelier Saturation index is applicable for all the samples. The pHs of 90% samples is lower than pH, hence the L.S.I. is positive in these cases, which reveals that the

Table 1. Physiochemical Characteristics of Underground Water from Hub Valley

Test	Samp 1	Samp 2	Samp 3	Samp 4	Samp 5	Samp 6	Samp 7	Samp 8	Samp 9	Samp 10	Samp 11	Samp 12	Samp 13	Samp 14	Samp 15	Samp 16	Samp 17	Samp 18	Samp 19	Samp 20
pH	6.68	7.00	7.00	7.00	6.93	7.11	7.05	6.95	6.59	6.65	7.52	8.08	7.88	7.05	7.96	7.64	7.93	8.26	7.4	7
Cnductivity (uS/cm)	3000	5520	3990	5110	3920	2583	2711	3690	3000	4610	4530	2770	2790	3500	2705	3440	4060	3680	2680	4340
TDS (ppm)	2130	2208	2833	2044	2783	1834	1925	2620	2130	3273	3216	1967	1981	2485	1921	2442	2883	2613	1903	3081
HCO_3^- (ppm)	240	298	239	150	179	300	298	269	119	478	180	60	160	179	419	299	359	197	239	178
HCO_3^- (me1/lit)	3.93	4.89	3.92	2.46	2.93	4.92	4.89	4.41	1.95	7.84	2.95	0.98	2.26	2.93	6.87	4.9	5.89	3.23	3.92	2.92
Cl^- (ppm)	689	1065	965	882	827	554	551	547		969	890	319	546	547	191	568	639	958	414	852
Cl^- (meq/lit)	19.14	30.00	27.18	24.85	23.30	15.61	15.52	15.41	15.49	27.30	25.07	8.99	15.38	15.41	5.38	16.00	18.00	26.99	11.66	24.00
SO_4^{--} (ppm)	330	620	519	659	371	350	292	276	473	597	721	370	406	535	576	742	762	618	372	453
SO_4^{--} (meq/lit)	6.88	12.92	10.81	13.73	7.73	7.29	6.08	5.75	9.85	12.44	15.02	7.71	8.46	11.15	12.00	15.46	15.88	12.88	7.75	9.44
Total Anion (Meq/lit)	30.22	47.80	41.91	41.03	33.96	27.82	26.49	25.57	27.30	47.57	43.04	17.68	26.46	29.49	24.25	36.36	39.76	43.09	23.33	36.36
Na^+ (ppm)	223	438	527	358	406	312	355	305	222	304	338	205	208	253	180	349	477	486	215	218
Na^+ (meq/lit)	9.70	19.04	22.91	15.57	17.65	13.57	15.43	13.26	9.65	13.22	14.7	8.91	9.04	11.00	7.83	15.17	20.74	21.13	9.35	9.48
K^+ (ppm)	4	12	11	13	14	9	10	10	17	14	17	4	7	14	7	8	8	7	3	9
K^+ (meq/lit)	0.10	0.31	0.28	0.33	0.36	0.23	0.26	0.26	0.44	0.36	0.44	0.1	0.18	0.36	0.18	0.21	0.21	0.18	0.08	0.23
Ca^{++}(ppm)	107	274	137	207	150	108	70	71	154	344	206	98	136	134	159	103	190	211	128	139
Ca^{++}(meq/lit)	5.35	13.7	6.85	10.35	7.50	5.40	3.50	3.55	7.70	17.30	10.30	4.90	6.80	6.70	7.95	5.15	9.50	10.55	6.40	6.95
Mg^{++}(ppm)	166	165	95	184	98	82	85	84	92	122	207	63	137	120	123	190	126	137	70	125
Mg^{++}(meq/lit)	13.83	13.75	7.92	15.33	8.17	6.83	7.08	7.00	7.67	10.17	17.25	5.25	11.42	10.00	10.25	15.83	10.50	11.42	5.83	10.42
Total Cation (Meq/lit)	28.98	46.80	37.96	41.58	33.68	26.03	26.27	24.07	25.45	40.94	42.68	19.17	27.44	28.06	26.21	36.36	40.94	43.28	21.66	27.08

Table 2. Thermodynamic Parameters of Underground water from Hub Valley

Test	Samp 1	Samp 2	Samp 3	Samp 4	Samp 5	Samp 6	Samp 7	Samp 8	Samp 9	Samp 10	Samp 11	Samp 12	Samp 13	Samp 14	Samp 15	Samp 16	Samp 17	Samp 18	Samp 19	Samp 20
C^1	1.75	1.66	0.84	1.83	0.92	2.01	1.93	1.2	1.75	0.08	0.18	1.90	1.89	1.34	1.94	1.39	0.76	1.17	1.95	0.43
pCa	2.57	2.16	2.47	2.29	2.43	2.57	2.76	2.75	2.41	2.07	2.29	2.61	2.47	2.47	2.40	2.59	2.32	2.28	2.49	2.46
pAlk	2.41	2.31	2.41	2.61	2.53	2.31	2.31	2.36	2.71	2.11	2.53	3.01	2.58	2.53	2.16	2.31	2.23	2.49	2.41	2.53
L.R.	6.68	8.78	9.7	15.69	10.57	4.66	4.42	4.8	12.99	5.07	13.59	16.97	9.09	9.05	2.53	6.42	5.76	12.34	4.95	11.46
pHs	6.72	6.14	5.71	6.72	5.88	6.88	7.00	6.3	6.87	4.25	5.00	7.52	6.94	6.35	6.50	6.29	5.32	5.94	6.85	5.42
L.S.I.	0.04	0.86	1.29	0.28	1.05	0.23	0.05	0.7	-0.28	2.40	2.52	0.56	0.94	0.70	1.45	1.35	2.61	2.32	0.55	1.58
ΔG (Kcal/mole)	0.06	-1.17	-1.75	-0.38	-1.43	-0.31	-0.06	-0.9	0.38	-3.27	-3.43	-0.77	-1.29	-0.96	-1.97	-1.84	-3.56	-3.16	-0.75	-2.15
R.S.C.	-14.91	-22.23	-10.66	-22.85	-12.53	-7.15	-5.53	-5.97	-13.23	-19.28	-24.18	-9.04	-15.32	-13.52	-1.08	-15.70	-13.86	-18.46	-8.17	-14.19
S.A.R.	3.16	5.17	8.49	4.38	6.35	5.52	6.77	5.82	3.50	3.59	3.99	3.98	3.02	3.83	2.61	4.7	6.60	6.42	3.8	3.24
E.S.P.	3.29	5.99	10.12	4.94	7.5	6.44	8.02	6.83	3.76	3.88	4.42	4.41	3.1	4.21	2.53	5.41	7.81	7.58	4.17	3.40
R.S.I.	6.67	5.28	4.42	6.44	4.83	6.65	6.95	5.57	7.15	1.85	2.84	6.96	6.00	5.65	5.05	4.94	2.71	3.62	5.3	3.84

underground water of Hub Valley is scaling in nature and the scaling of 65% samples is in moderate range. The corrosion / scaling trend of underground water of Hub Valley on the basis of L.S.I. values is graphically shown in Fig. (**1**).

The values of Ryznar Stability Index of all the water samples except sample number 9 lie below 7. This also indicates that this underground water of Hub Valley is scale forming not corrosive Fig. (**2**) depicts these results.

The values of free energy change ΔG were also calculated. 90% values are on negative side, which further indicates that the underground water of Hub Valley is scale forming. Only sample No.1&9, are low and moderately

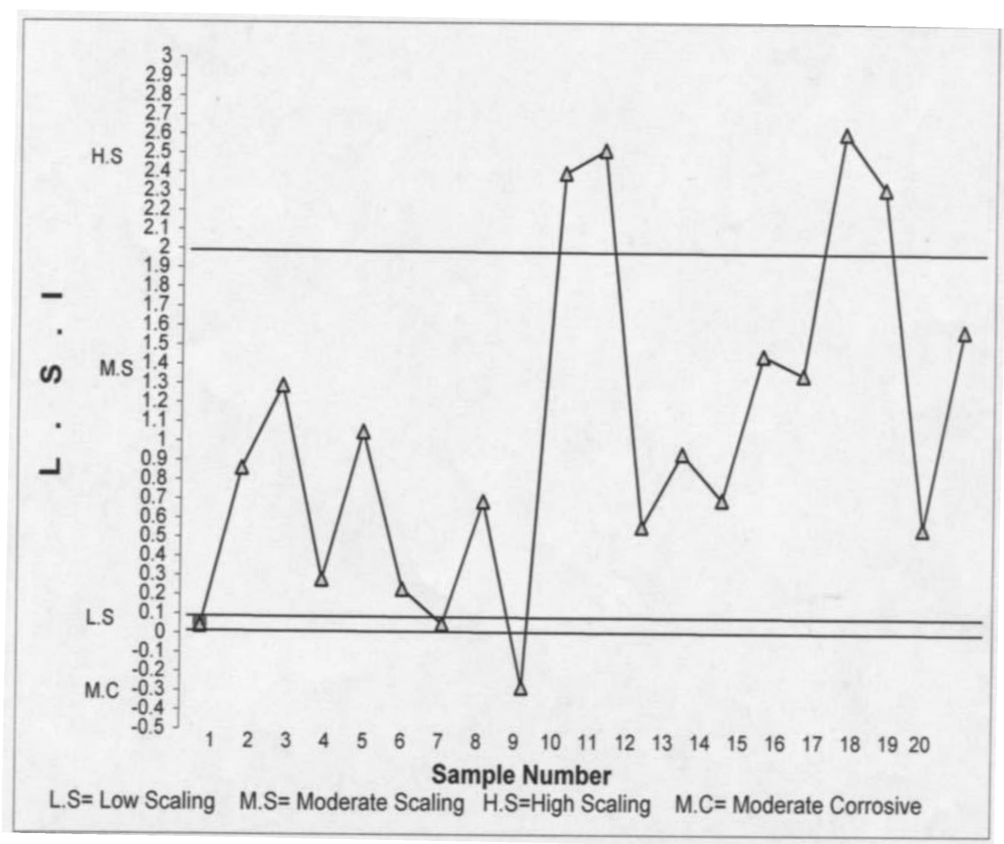

Fig. (1). Corrosive/scaling trend of under groundwater of Hub Valley on the basis of L.S.I. values.

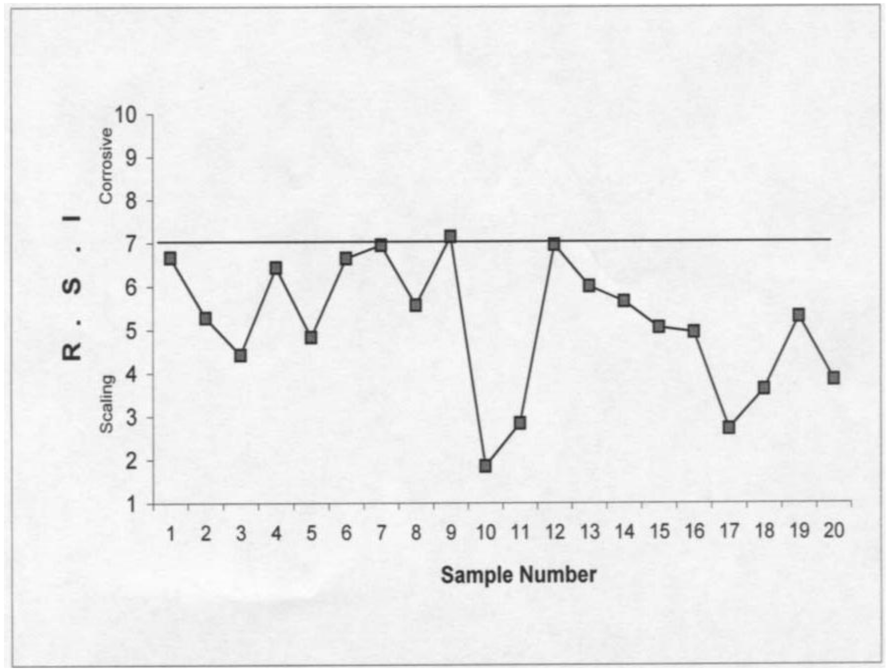

Fig. (2). Corrosive/scaling trend of under groundwater of Hub Valley on the basis of R.S.I. values.

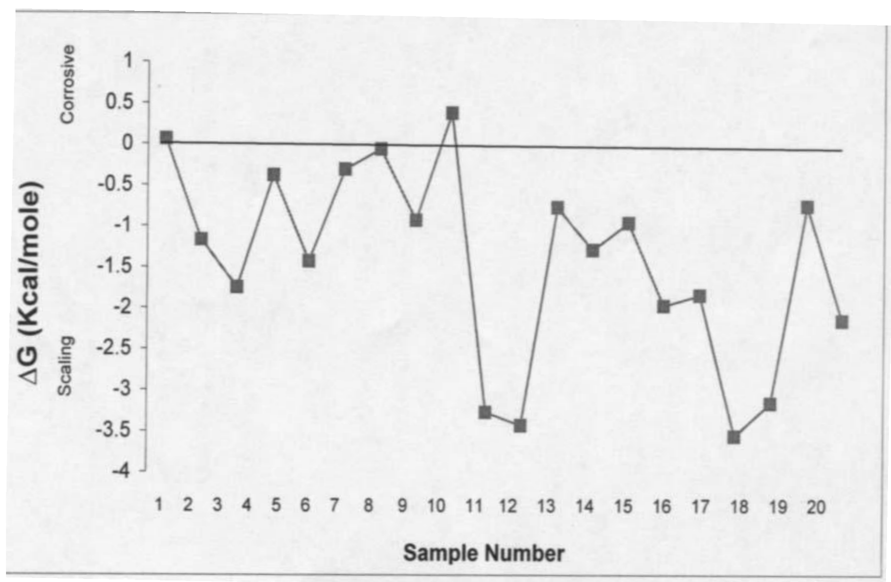

Fig. (3). Corrosive/scalling behaviour of underground water of Hub Valley on the basis of free energy (ΔG)

corrosive respectively. All other samples are scale forming in nature. These results are graphically shown in Fig. (**3**).

Small amount of scale formation is not always a bad thing. In some cases, a thin layer of $CaCO_3$ scale helps to inhibit corrosion. Moreover, viable treatment alternatives to prevent scale formation or remove existing scale, includes acid neutralization, chemical antiscalents, water softening devices and magnetic flow through or non-intrusive devices DeGiorgio [5].

CONCLUSION

Analysis of thermodynamic parameters reveals that the underground water of Hub Valley is scale forming in nature. However it can safely be used by applying viable treatment alternatives.

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