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Effect of Various Impurities on the Hardness of NaCl Crystals

The hardness of NaCl crystal in the presence of mono, divalent and polyvalent ions were measured. Measurements were made in the indentation load range from $5x10^{-3}$ to $20x10^{-3}$ N. The measured data showed that there is an indentation size effect. Classical Meyer's law was used for the characterization of crystal hardness of NaCl. The Meyer index was found to be smaller than 2 indicating brittle material characteristic. The PRS model was also used for the determination of the load-independent microhardness value. It was found that the crystal hardness of NaCl is chancing depending on the type of impurity and the concentration.

Keywords: impurity, vickers microhardness, indentation size effect, crystal hardness

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1. Introduction

The crystalline products are mainly characterized by purity and crystal size distribution (CSD) which are determined by kinetic and mechanical parameters. Secondary nucleation is one of the most important kinetic parameters but it is influenced also by mechanical parameters. Under most commercial operation conditions, secondary nucleation is unavoidingly taking places in the crystallizer, depending on the local fluid dynamic conditions inside the crystallizer, the attrition behaviour of crystalline material and growth of the attrition fragments. Especially hydrodynamic effects such as crystal-crystallizer and crystal-crystal collision makes the secondary nucleation the dominant nucleation mechanism in crystallizer. In general, the secondary nuclei exhibit anomalous growth behaviour and cause growth rate dispersion (GRD) (GARSIDE et al). On the other hand, the GRD considerably influence the CSD and plays an important role in establishing the actual CSD in crystallizer. The changes of CSD in crystallizer affects the product properties such as filterability, dryability, flowability etc. Additives and impurities are also important on the formation of CSD, because they can change the kinetics of nucleation, crystal growth, and also the secondary nucleation phenomena. They can also modify the important properties of the crystalline material such as crystal hardness, crystal habit, bulk density, powder flow characteristics etc. Crystal hardness is a measure of the resistance of the local deformation. Consequently, the knowledge of the hardness of crystals gives important information for the understanding of the nature of secondary nucleation phenomena. Recently several workers (JOHNSTON; PRATAP et al.) have investigated the effect of the some impurities on the microhardness of potassium chloride and ammonium halides. They showed that the divalent impurities have a strong effect on the mechanical properties of the investigated crystals. A number of the workers (OFFERMANN, ULRICH; ULRICH, KRUSE 1990; ULRICH, KRUSE 1993) also showed that the hardness of crystals may be an approach for description of the abrasion resistance of salts. In order to understand more about the use of crystal hardness for prediction of secondary nucleation phenomena, the relationship between the impurity and crystal hardness must be known. Based on the above arguments, NaCl was selected as model substance and the effect of monovalent, divalent and trivalent ions on the crystal hardness of NaCl was investigated.

Table 1: Microhardness of NaCl crystals as a function of the load range in the presence of K^+ and Co^{+2} ions.

Impurity Concentration (ppm)	K^+ Applied Load (N)			Co^{+2} Applied Load (N)		
	$5x10^{-3}$	$10x10^{-3}$	$20x10^{-3}$	$5x10^{-3}$	$10x10^{-3}$	$20x10^{-3}$
0	281.4	244.3	226.1	281.4	244.3	226.1
1	239.2	229.5	208.4	261.5	245.1	217.6
2	237.3	231.4	207.8	261.8	249.0	218.6
3	238.3	229.4	208.8	263.7	246.1	218.5
4	239.2	229.5	208.8	262.7	245.1	219.6
5	241.2	231.4	210.8	263.0	245.8	220.3
10	243.0	233.0	212.3	264.7	230.7	220.5
25	242.1	234.3	213.7	264.9	246.3	223.0
50	243.1	234.4	214.7	265.2	247.5	224.4
100	237.0	234.1	215.5	266.98	247.9	226.6

Table 2: Microhardness of NaCl crystals as a function of the load range in the presence of Ni^{+2} and Cu^{+2} ions.

Impurity Concentration (ppm)	Ni^{+2} Applied Load (N)			Cu^{+2} Applied Load (N)		
	$5x10^{-3}$	$10x10^{-3}$	$20x10^{-3}$	$5x10^{-3}$	$10x10^{-3}$	$20x10^{-3}$
0	281.4	244.3	226.1	281.4	244.3	226.1
1	268.3	245.2	219.7	256.8	244.3	218.5
2	265.9	243.3	218.1	290.2	261.8	236.1
3	278.6	238.6	217.7	316.7	321.2	281.7
4	275.2	239.9	215.8	274.5	269.2	262.7
5	274.7	239.4	213.7	285.3	269.2	258.6
10	273.2	233.4	211.1	248.6	238.6	224.7
25	281.0	233.0	211.8	241.4	233.5	218.7
50	278.5	223.4	209.1	249.8	229.8	213.7
100	275.5	219.6	205.9	239.8	226.1	206.5

2. Experimental

All solutions were prepared using distilled water and analytical grade substances. Saturated NaCl solution was prepared at 25°C according to the solubility data (SEIDEL, LINKE) and known amounts of impurities were added to the solution. Then the solution was filtered using a membrane filter (Millipore 0.45 µm pore size). KCl, $PbCl_2$, $CrCl_3 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 6H_2O$ and $FeCl_3 \cdot 6H_2O$, were used as impurities. The pure and impure sodium chloride crystals were prepared by slow evaporation (25°C) in aqueous solution. The impurity concentration range in solution was varied from 0 to100 ppm. Transparent crystals free from cracks were selected for microhardness measurements. The Vickers hardness indentations were carried out on the as-grown (100) surface of the NaCl crystals. Microhardness of pure and impure sodium chloride crystals were measured at room temperature in the indentation load range from $5x10^{-3}$ to $20x10^{-3}$ N using an ultra microhardness tester produced by Anton Paar Company. The Vickers's diamond pyramidal intender is attached to microscope with an adapted video camera in order to measure the indentations on a monitor. The indentation time was selected to 10 s. At least 10-15 indentations were made and the mean arithmetic values of the measured two diagonals were used for the calculation of hardness. The Vickers hardness number H_v was calculated from Eq.1:

$$Hv = 1{,}8544 \frac{P}{d^2} \tag{1}$$

where P is the indentation force in Newton, d is the average diagonal length (mm) and 1.8554 is a constant of a geometrical factor for the diamond pyramid.

Table 3: Microhardness of NaCl crystals as a function of the load range in the presence of Cr^{+3} and Fe^{+3} ions.

Impurity Concentration (ppm)	**Cr^{+3}** Applied Load (N)			**Fe^{+3}** Applied Load (N)		
	$5x10^{-3}$	$10x10^{-3}$	$20x10^{-3}$	$5x10^{-3}$	$10x10^{-3}$	$20x10^{-3}$
0	281.4	244.3	226.1	281.4	244.3	226.1
1	270.4	232.8	223.2	281.4	253.2	233.1
2	271.0	225.8	221.1	268.7	251.5	229.0
3	255.7	227.1	215.9	277.6	237.8	232.7
4	257.1	243.7	214.7	271.7	237.0	223.3
5	261.1	231.9	213.7	270.0	239.7	217.0
10	260.0	226.7	213.7	278.4	234.3	218.4
25	236.4	241.9	214.5	277.5	237.9	217.6
50	265.8	238.4	213.5	277.8	237.8	216.8
100	266.2	235.8	208.6	276.5	233.3	212.7

3. Results and Discussion

The crystal hardness of pure and impure NaCl were measured at three different indentation loads. The results are given in Tables 1 to 3. As can be seen from Tables 1 to 3 the microhardness value of NaCl shows a dispersion at $5x10^{-3}$ N. During the microhardness measurement it was observed that in a low load range the same crystals shows different hardness values. In general, there are two possible factors which may effect the preciseness of the hardness measurement. The first is the optical resolution of the objective lens which is used for measuring the diagonal length. The second is the surface stress of crystal. Normally, the stress is in a very thin layer on the crystal surface but it becomes important especially at very low load ranges. Consequently, both factors together affect the measurement and causes to find a widening of hardness distribution. On the other hand, as can be seen from Tables 1 to 3, at high load ranges, NaCl crystals have a low microhardness value. All the impure NaCl crystals studied here show also the same behaviour. In solid mechanics, the material hardness is described as the resistance to deformation and it should be independent from the applied load. However, a number of workers reported that the hardness of materials changes depending on the applied loads, especially at small load ranges. As can obviously be seen from Tables 1 to 3 that the crystal hardness of NaCl is load depending and the value of the hardness decreases with increasing load applied. It is clear that, there is a indentation size effect (ISE) on the measurement. In order to analyze the ISE in the hardness testing it needs to fit the experimental data according to the Meyer's law (MEYER) which correlate the applied load P the resulting indentation size d with each other:

$$P = Ad^n \tag{2}$$

where A is constant parameter for a given material and n is the Meyer index. These parameters are derived from the curve fitting of experimental results of indentations. The value of n is nearly equal to 2. However, n is usually found as less than 2 especially in the low load hardness region. Plots in which load P versus indentation the diagonal d in a log-log scale were drawn for pure and all impure crystals examined. Table 4 summarizes the Meyer law parameters determined in different load ranges for each impurity concentration. As can be seen in Table 4, the values of n lies between 0.534 - 0.6050. It means NaCl shows a brittle material characteristic. The Meyer law is simply an empirical expression to describe the relationship between indentation load and the resultant indentation size. It gives suitable results only in a narrow range of indentation loads. The Meyer's parameters were used for the characterization of the experimental data, however, it was found that the classical Meyer law is insufficient for the description of our experimental data. It is more suitable to use a polynomial equation for representation of experimental data. Recently a number of workers (LI, BRADT; FRÖHLICH et al.) explain the indentation size effect with the proportional specimen resistance (PRS) model. According to the PRS model, microhardness can be described with two components, the first term represents the resistance of the test specimen to elastic deformation and friction at the indenter/specimen facet interface or ISE regime and the second term represents the load independent part (LI, BRADT). The indentation load P is related to the indentation size d as follows:

$$P = a_1 d + a_2 d^2 \tag{3}$$

and Eq.3 can be transformed into:

$$\frac{P}{d} = a_1 + \left(\frac{P_c}{d_0^2}\right) d \tag{4}$$

where a_1 is a constant parameter, P_c is the applied load at which microhardness becomes load independent and d_0 is the diagonal length of the indentation. The parameters a_1 and $\frac{P_c}{d_0^2}$ are included in Eq.4 and can be evaluated through the linear regression of P/d versus d. The load independent microhardness value can be calculated by using the Vickers conversion factor 1.8544.

$$\text{Hv} = 1.8544 \times \frac{P}{d_0^2} \tag{5}$$

Table 4: Meyer's law parameters determined in the presence of different impurities and concentration

Imp. Conc. (ppm)	A						n					
	K^+	Co^{+2}	Ni^{+2}	Cu^{+2}	Cr^{+3}	Fe^{+3}	K^+	Co^{+2}	Ni^{+2}	Cu^{+2}	Cr^{+3}	Fe^{+3}
0												
1	0.114	0.119	0.121	0.115	0.121	0.116	0.549	0.566	0.572	0.558	0.569	0.568
2	0.113	0.118	0.122	0.118	0.124	0.112	0.547	0.565	0.571	0.574	0.573	0.557
3	0.03	0.119	0.131	0.095	0.118	0.116	0.545	0.567	0.589	0.542	0.569	0.493
4	0.114	0.118	0.132	0.089	0.119	0.121	0.549	0.565	0.589	0.515	0.565	0.570
5	0.113	0.117	0.133	0.098	0.124	0.126	0.48	0.564	0.590	0.536	0.572	0.578
10	0.113	0.119	0.135	0.105	0.124	0.131	0.550	0.565	0.593	0.536	0.571	0.587
25	0.111	0.116	0.140	0.105	0.124	0.131	0.545	0.562	0.602	0.535	0.574	0.588
50	0.110	0.115	0.143	0.116	0.127	0.132	0.545	0.561	0.603	0.556	0.579	0.589
100	0.102	0.114	0.145	0.116	0.133	0.129	0.534	0.559	0.605	0.554	0.588	0.594

Table 5: PRS model parameters and load independence microhardness values determined in the presence of K^+ and Co^{+2} ions.

Impurity Concentration (ppm)	$\mathbf{K^+}$			$\mathbf{Co^{+2}}$		
	a_1	P_c/d_0^2	Hv^*	a_1	P_c/d_0^2	Hv^*
0	0.306	97.93	181.6	0.306	97.93	181.6
1	0.214	97.09	180.04	0.281	96.68	179.28
2	0.215	97.01	179.89	0.285	97.11	180.01
3	0.207	97.87	181.49	0.286	96.76	179.43
4	0.211	97.50	180.80	0.273	98.15	182.01
5	0.210	98.54	182.73	0.271	98.64	182.91
10	0.217	98.83	183.27	0.245	99.40	184.32
25	0.201	100.84	186.99	0.261	100.62	186.59
50	0.198	101.47	188.16	0.258	101.44	188.11
100	0.163	104.70	3193.73	0.249	103.17	191.32

Table 6: PRS model parameters and load independence microhardness values determined in the presence of Ni^{+2} and Cu^{+2} ions.

Impurity Concentration (ppm)	$\mathbf{Ni^{+2}}$			$\mathbf{Cu^{+2}}$		
	a_1	P_c/d_0^2	Hv^*	a_1	P_c/d_0^2	Hv^*
0	0.306	97.93	181.6	0.306	97.93	181.6
1	0.294	96.36	178.69	0.255	99.12	183.88
2	0.292	95.74	177.54	0.310	103.20	191.37
3	0.334	91.61	169.88	0.249	132.21	245.17
4	0.339	90.55	167.91	0.075	133.35	247.28
5	0.346	89.19	165.39	0.162	125.64	232.98
10	0.344	87.71	162.65	0.159	109.15	202.41
25	0.369	85.79	159.08	0.157	106.38	252.90
50	0.365	84.45	156.60	0.224	98.41	182.49
100	0.361	82.98	153.87	0.223	95.27	176.66

Table 7: PRS model parameters and load independence microhardness values determined in the presence of Cr^{+3} and Fe^{+2} ions.

Impurity Concentration (ppm)	**Cr^{+3}**			**Fe^{+3}**		
	a_1	P_c/d_0^2	Hv^*	a_1	P_c/d_0^2	Hv^*
0	0.306	97.93	181.6	0.306	97.93	181.6
1	0.257	99.60	283.69	0.276	103.95	192.76
2	0.261	97.65	181.08	0.248	104.62	194.01
3	0.229	98.57	182.78	0.235	105.66	195.93
4	0.280	65.46	121.39	0.268	99.15	183.86
5	0.276	64.26	119.16	0.307	93.74	173.83
10	0.262	94.89	175.96	0.322	92.48	171.49
25	0.302	93.38	173.16	0.330	91.76	170.16
50	0.311	91.96	170.53	0.335	91.14	169.01
100	0.338	87.52	162.29	0.349	88.13	163.42

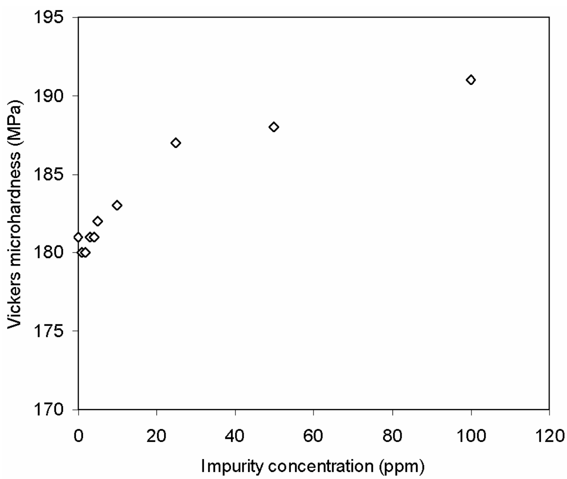

Fig. 1: The influence of K^+ ions on the Vickers microhardness of NaCl

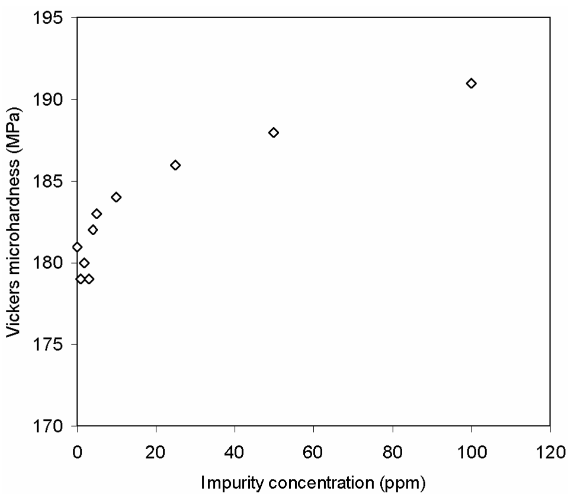

Fig. 2: The influence of Co^{+2} ions on the Vickers microhardness of NaCl

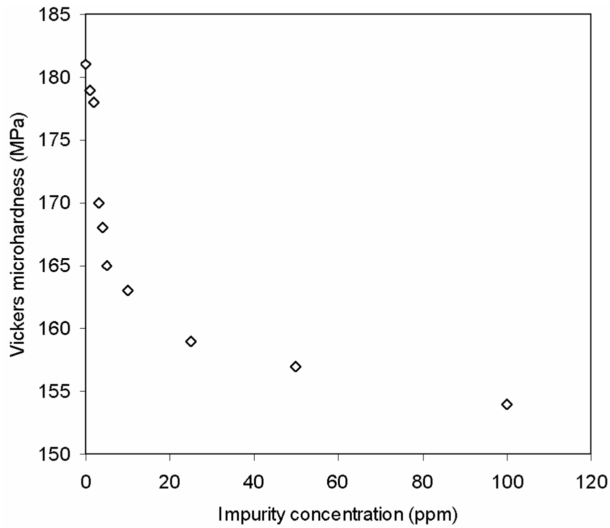

Fig. 3: The influence of Ni^{+2} ions on the Vickers microhardness of NaCl

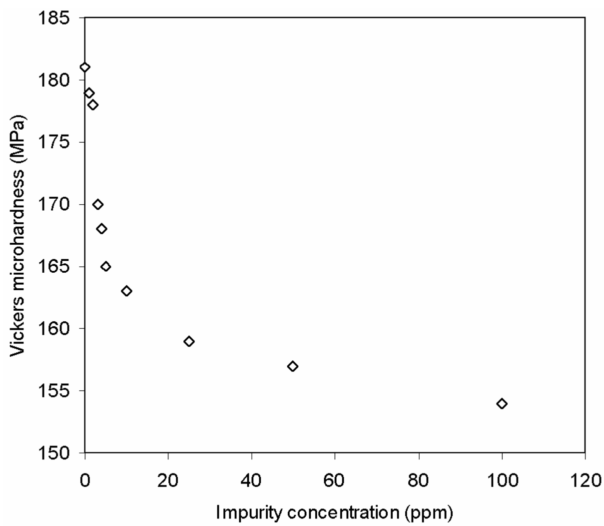

Fig. 4: The influence of Cu+2 ions on the Vickers microhardness of NaCl

The experimental data obtained from the microhardness measurement again were analyzed according to Eqs.4-5, and results are listed in tables 5-7. All results found have a correlation factor 0.999. Tables 5 to 7 presents that the microhardness of NaCl is significantly depending on the impurity type and the concentration. The variation of Vickers hardness of NaCl crystals with impurity concentration are given in Figs. 1 to 7. As can be seen from Table 1, the Vickers hardness of pure NaCl crystals was found to 181 MPa. This value has been given in literature between the 170 and 240 MPa (ENGELHARDT et al.; PLENDL et al.; CHIN; GHAN; ULRICH 1990). Microscopic observations of pure NaCl crystals showed that around room temperature (25 °C) NaCl crystals grow in a perfect cubic form and without crack formation. It was also observed that NaCl crystals grown from pure solution layer by layer from center to corners.

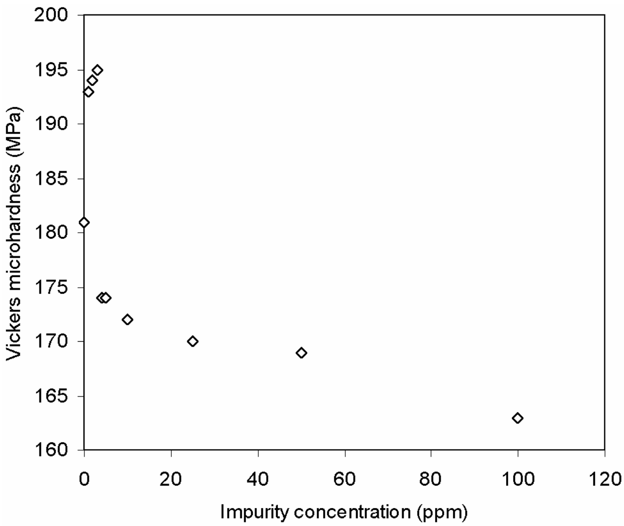

Fig. 5: The influence of Fe^{+3} ions on the Vickers microhardness of NaCl

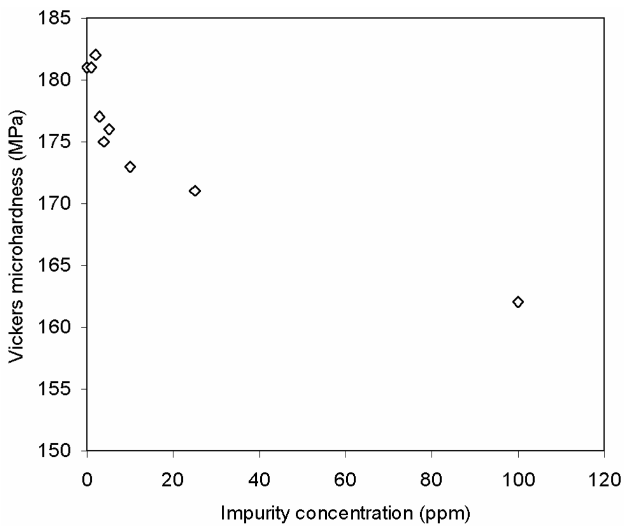

Fig. 6: The influence of Cr^{+3} ions on the Vickers microhardness of NaCl

Figs. 1 and 2 present the effect of K^{+} and Co^{+2} ions on the Vickers hardness of NaCl crystals. As to be seen from Figs.1 and 2, in the presence of both impurities, the crystal hardness of NaCl is increased with increasing impurity concentration. Microscopic observations showed that in the presence of K^{+} ions, the crystals tend to grow layerwise from center to corners. The inclusion formation and crack formation was not observed at all investigated concentration range. In the presence of Co^{+2} ions, the step generation was observed in the edge of crystals. It was also observed that there is a significant crack and inclusion formation in the different parts of crystals. These effects was found dominant especially above the 25 ppm Co^{+2} ions. Figs. 3 and 4 show the effect of Ni^{+2} and Cu^{+2} ions on the Vickers hardness of NaCl crystals. At small impurity concentrations (0 to 5 ppm) the crystal surface of NaCl was formed nearly flat but increasing Ni^{+2} ion concentration, the crystal surface was changed and a box-like crystal surface was formed. The formation of this type of surface is due to the effect of the retaining of growth sites.

In the presence in 0 to 4 ppm Cu^{+2} ions, there are noticeable increases in the hardness of NaCl crystals. By addition more than 4 ppm Cu^{+2} ions to crystallization media, there is a gradual decreasing in the crystal hardness of NaCl. Microscopic observations of crystals showed that above the 25 ppm Cu^{+2} ions, there are step generation on the edge of crystals and also cavity formation in the center of crystals. It was also observed that there is a significant formation of inclusion and crack.

Figs. 5 and 6 show the effect of Fe^{+3} and Cr^{+3} ions on the Vickers hardness of NaCl crystals. In the presence of 0 to 3 ppm Fe^{+3} ions, the crystal hardness of NaCl is increased sharply and with more than 3 ppm Fe^{+3} ions the crystal hardness is decreased sharply again. A similar situation was found also for Cr^{+3} ions. In the presence of all investigated Fe^{+3} ion concentrations, only thin surface layer growth was observed. The crystal color also was changed from colorless to yellow as a function of Fe^{+3} ion concentration. In the presence of Cr^{+3} ions step generation on the edge of crystal and cavity formation in the center of crystal were formed. It was also found that there is an effective crack and inclusion formation on the different parts of the crystals.

Microscopic observations of all examined crystals showed that the crystal surface form was changed as a function of impurity type and concentration. In general, the effect of impurities on crystal formation are not predictable and mostly, it is highly depend on the type of the interaction between the crystal surface and impurity molecules. As a general law, the impurities are adsorbed preferentially on the crystal surface where the free adsorption energy is a minimum. The coverage of crystal faces by impurities causes a reduction in growth rates and/or a formation of different surface phenomena such as cavities, inclusions etc. On the other hand the supersaturation and hydrodynamic conditions are also important for the formation of crystal forms. The mechanism and the factors which are effecting the formation of these phenomenon have been given in literature (DENBIGH, WHITE; BUNN).

4. Conclusion

The hardness of NaCl crystal was examined in the presence of mono, divalent and trivalent ions. It was shown that, the crystal hardness of NaCl is load dependent. The classical Meyer's law and PRS models were used for characterization of the measured data. It was also shown that the PRS model is more suitable for the data characterization. On the other hand, it was found that the crystal hardness of NaCl was changed depending on the type of impurities and concentrations. In the presence of all impurities, NaCl crystals show brittle material characteristics. Microscopic observations of crystals were briefly explained. It was found that in the presence of Cu^{+2}, Co^{+2} and Cr^{+3} ions there is step generation, cavity, crack and inclusion formation. The change of the impurity concentration also induced the formation of growth steps and changes of the velocity of the steps.

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