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TECHNICAL ARTICLE

Geochemical Effects of Increased Production on Recirculated Process Water at the Kiirunavaara Iron Mine, Northern Sweden

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Abstract Understanding process water characteristics and variations is important for ensuring high quality processing of iron ore. Large amounts of water are used during refinement, and the water is often recirculated to save energy. Water quality is important for processes such as flotation and agglomeration but recirculation of process water and changes in production can alter water quality significantly. This study was undertaken to better understand the origin of dissolved components in the process water and water quality variations in process water geochemistry at the Kiirunavaara magnetite ore mine, based on analyses from 1989 to 2008. Long-term trends at single sampling stations in the process chain, as well as changes along the process chain, were studied. Ca, S, Na, and Cl are the major elements in the process water, accounting for over 80% of the dissolved concentration. Ca has the highest concentrations with a mean of 183 mg/L and a maximum of 303 mg/L in the clarifying pond. At all investigated sampling stations (influent water and water in the sorting plant, concentration plant, pelletizing plant, and clarifying pond), dissolved elemental concentrations increased during the studied time period. This increase was mainly caused by increased production. The high concentrations of Ca and S probably result from sulfide oxidation and calcite buffering in the drainage area. The high N concentrations come from undetonated explosives while the main source of Na and Cl is fluid inclusions. If production continues to increase, higher concentrations in the process water should be anticipated.

Keywords Calcium · Flotation · Fluid inclusions · Kiirunavaara · Magnetite · Process water

Introduction

A large amount of process water is used during the refinement of ore in the mining industry. However, today much of the process water is recirculated to save energy and water. The process water mainly acts as a transport medium but it is also needed in the refinement process, for example, in flotation. In a study of the process water at the Kiirunavaara magnetite ore mine in northern Sweden (Fig. 1) Lundkvist (1998), found that the concentration of totally dissolved elements ranged from 1,000 to 1,900 mg/L. In that study, the large variation in concentrations was partly explained by seasonal changes and an increase in production. Increasing amounts of freshly milled particles in contact with the recirculated process water might have increased element concentrations. The large variations in process water quality seen in Kiirunavaara could influence the process quality and the end product, iron ore pellets (Lundkvist 1998).

Two process steps where the process water quality is of special interest are flotation and balling. Engesser (2003) showed that pellet strength is affected by the divalent ion concentration in the process water. This was partly explained by the fact that the swelling capacity of bentonite, which is used as a binder, is reduced if the process water has a high concentration of Ca ions. In the flotation step, the ion concentration affects, among other things, the effectiveness of dispersion and flocculation of iron ore (Arol and Iwasaki 2003). The different elements, mostly ions, can have a huge impact on flotation performance due to changes in parameters such as pH and mineral surface

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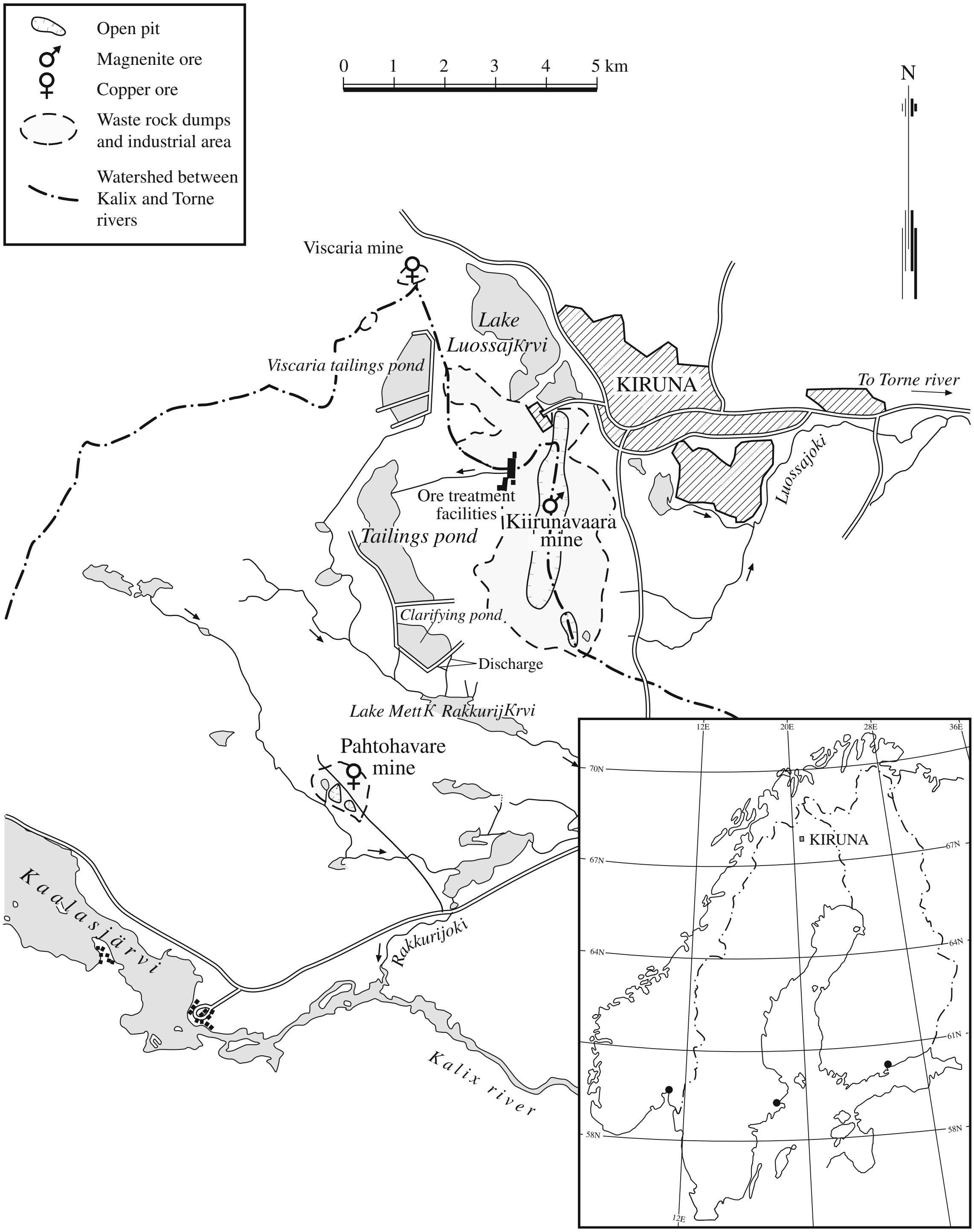

Fig. 1 Location of Kiruna and the ore treatment facilities

characteristics (Rao et al. 1989; Qi et al. 1993). It is thus important to understand what regulates the process water quality and how it varies. It is also important to understand process water variations to keep environmental impacts low. For example, high levels of nitrogen in the water discharged downstream could lead to eutrophication, and high levels of sulfur from evaporated process water (during sintering) could lead to acid rain (Likens et al. 1996; Mattila et al. 2007).

To get a better understanding of what affects water quality at Kiirunavaara, this study used data from a process water sampling program stretching from 1989 to 2008.

Possible effects from increased production were also investigated using a simple regression model.

The Kiirunavaara Magnetite Ore Mine

The Kiirunavaara apatite iron ore body contains c. 2,000 Mt of iron ore of 60–68% Fe, and strikes in a N–S direction. It is c. 5 km long, up to 100 m thick and extends at least 1,300 m below the surface. The ore follows a thick sequence of c. 1.9 Ga old trachyandesitic lavas (traditionally called syenite porphyry) and overlying pyroclastic rhyodacites (traditionally called quartz-bearing porphyry). Magnetite-actinolite breccia is developed in both the footwall and the hanging wall (Bergman et al. 2001). The phosphorus content of the ore exhibits a pronounced bimodal distribution with either less than 0.05% P or more than 1.0% P. The magnetite is mostly very fine grained but in the central part of the apatite pore ore, coarser magnetite up to 2 mm in size may occur, together with calcite and small amounts of pyrite (Bergman et al. 2001). Hornblende is a common gangue mineral and calcite, biotite, quartz, titanite, and albite occur (Parák 1975). For a chemical description of the apatite and magnetite in Kirunavaara, see Harlov et al. (2002). Blake (1992) described the hanging wall and foot wall mineralogy. The dominating mineral was alkali feldspar (about 50% by volume), followed by hornblende (2–35%), lesser amounts of actinolite, albite, quartz, K-feldspar, and magnetite, and traces of pyroxene, biotite, muscovite, titanite, fluor-apatite, and zircon, and an alteration assemblage of chlorite epidote, calcite, and sericite. Chemical analyses performed by Blake (1992) gave CaO and MgO levels of about 4 wt%.

The mine was opened in 1898, and is today operated by the mining company Lousavaara-Kirunavaara Aktiebolag (LKAB). Until the late 1950s, the ore was extracted mainly by open pit mining. Since then, Kiirunavaara has been an underground mine. The main end product at Kiirunavaara is iron ore pellets.

The process water at the Kiirunavaara mine is recirculated in the process chain, and only about 20% leaves the system. It is replaced with drainage water and groundwater pumped up from the mine. The high degree of recirculation means that all additives and chemicals in contact with the process water affect the process water quality over the entire process chain. The main additives in the processes are olivine, dolomite, lime, quartzite, bentonite, sodium silicate, sodium hydroxide, flotation agent (Atrac 1563), and methyl isobutyl carbinol (Sundquist and Adolfsson 2004).

The Process Water System

A simplified sketch of the process water system at the Kiirunavaara magnetite ore mine is shown in Fig. 2. Several smaller flows exist, but the main transport routes are drawn. Groundwater enters the system at the mine (sampling station KP 27), and from there the water is pumped up to a reservoir. Water is also pumped into that reservoir from the clarifying pond (KP 4). Most of the water in the clarifying pond comes from the different processing plants but rain, snow, and groundwater also flow into the pond. From the reservoir, water is pumped to the different processing plants. The processing plants also have an internal (inner) water processing system; water from the processing plants goes to the thickeners, which both dewater the tailings and deslime the circulating water, and then the water is pumped back to the processing plants.

The process water sampling stations are located at KP 27, KSret, KA 1ret, KA 2ret, KK 3ret and KP4 (see Fig. 2),

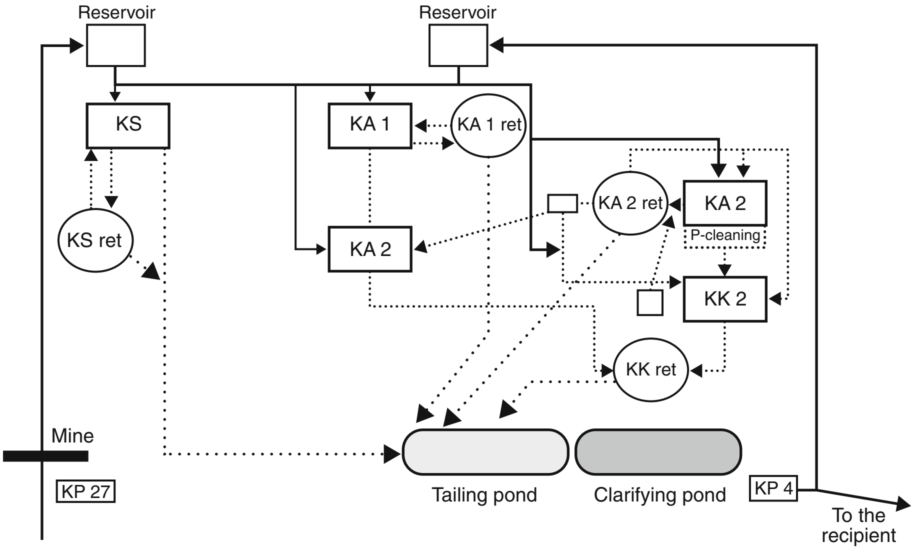

Fig. 2 Schematic flow sheet of the LKAB process water system at the Kiirunavaara iron ore mine. The abbreviations are: KP27—The last pumping station in the drainage chain of the mine, KP4—Pumping station for recirculation of water from the pond system, KS—sorting plant, KA1 and KA2—Concentrating plants, KK2 and KK3—pelletizing plants, KSret—thickener and the inner water system supporting KS, KA1ret, KA2ret and KKret thickeners and inner water systems supporting KA1 and KA2, KK2, KK3 respectively

and are named KVA 33, KVA 114, KVA 116, KVA 118, KVA 120, and KVA 001, respectively. KVA 001 is located at the end of the clarifying pond.

Major Changes in the Process Water System during the Sampling Period

In 1995 a new concentrating plant, KA 2, and a new pelletizing plant, KK 3, were started. The increased production was mainly supported by an increase in recirculation of the process water in the inner system.

Short Description of the Different Processing Plants

Sorting plant (KS): The iron ore is pre-crushed to different sizes before it is transported to the concentration plants. Most of the processes here are dry.

Concentration plants (KA 1 and KA 2): The crushed iron ore is milled and separated with wet magnetic separation. The water flows through a flotation step where Atrac (a flotation agent) and Na-silicate are added. The tailings are transported to a thickener from which the overflow water is reused in the process. The tailings are then transported to the tailings pond. KA 1 and KA 2 share recirculated water, but a larger share is transported to KA 1. Sometimes, additives such as olivine, dolomite, and calcite are used here to meet specific product requirements.

Pelletizing plant (KK 3): In the pelletizing plant, the iron ore concentrate is dewatered and balled after the addition of binders; bentonite is the main binder.

Methods

Sampling

All sampling used in this study was performed by personnel stationed at the Kiirunavaara production site, mainly for their annual environmental report. Only the clarifying pond (KVA001) has been sampled regularly since 1989. The other sampling stations were sampled from 2004 to 2006.

Membrane Filtration

The water samples were filtrated through 0.45 μm Sartorius membrane filters with a diameter of 142 mm.

Chemical Analyses

All samples were analyzed by ALS Scandinavia in Luleå, accredited according to ISO international standards 17025, ISO 9001:2000, SS EN 1484, and ISO/IEC Guide 25. For water samples, 1 mL of HNO_3 was added for every 100 mL of sample. The samples were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma sector field mass spectrometry (ICP-SFMS). Nitrogen was analyzed by a FIASTAR 5000 at the accredited lab at LKAB. Conductivity and pH also have been measured on a regular basis.

Statistical Analyses

Statistical analyses were conducted using the Statistica computer program (StatSoft 2008).

Results and Discussion

The clarifying pond, sampling station KVA 001, where sampling has been ongoing from 1989, provides a good overview of long-term and seasonal changes. Electrical conductivity is an indirect measure of total ion concentration, which makes it a useful tool to study changes. Variations in the electrical conductivity for the process water are shown in Fig. 3. A clear increasing long-term trend is obvious, despite large seasonal variations. Mean, minimum, and maximum values of electrical conductivity and elemental concentrations for the sample period are shown in Table 1. During the sampling period, Ca showed the highest mean concentration, 183 mg/L, and the highest maximum concentration 303 mg/L, followed by S with 162 and 292 mg/L, Cl with 132 and 250 mg/L, and Na with 88 and 172 mg/L. Although S was measured as an elemental concentration, it occurs as sulfate in the process water.

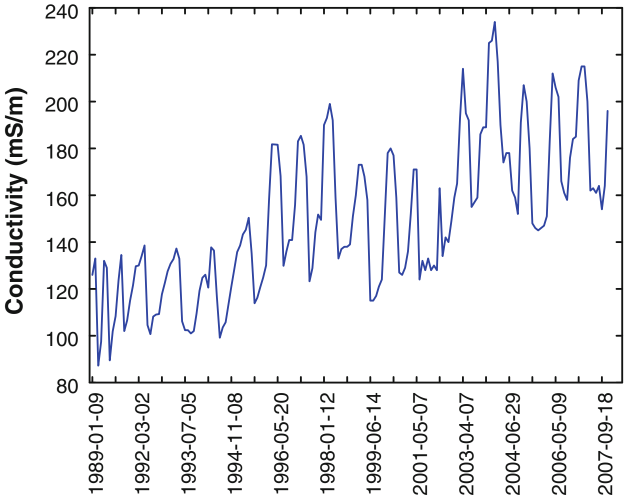

Fig. 3 Variations of electrical conductivity over time at sampling point KVA 001, the clarifying pond

Table 1 Element concentrations in mg/L and conductivity in mS/m at sampling point KVA 001, the clarifying pond

	# of samples	Mean	Minimum	Maximum
Conductivity	179	149	87	234
Ca	164	183	113	303
S	163	162	106	292
Na	164	88	47	172
Cl	154	132	60	250
Mg	164	22	13	35
K	164	37	20	63
Si	158	5	0.35	10
N	179	15	7.2	30
Sr	156	0.6	0.4	1.0
pH	148	7.9	7.2	9.2

These ions account for over 80% of the analytes in the process water.

Seasonal Variations

The seasonal variations of electrical conductivity seen in Fig. 3 mainly consist of a dilution period during snow melt, and then an increase that ends just before the snow melt starts again. Dilution should affect elemental variations for all elements in the same way. As can be seen in Table 2, electrical conductivity correlates well with all of the elements, and that a strong correlation exists between the different elements.

Principal component analysis (PCA) is useful in understanding and visualizing variations (Johnson 1998). The PCA on the correlation matrix for all of the data (shown as mean values in Table 3) shows that one factor explains more than 90% of the variation at KVA001 (with no rotation) in the PCA (Fig. 4). All other factors have Eigen values far below 1, which means that they have little explanatory value and could be pure noise (Johnson 1998). When all elements cluster like this on one factor, it is clear that the dilution effect discussed above is responsible for most of the variation.

Long Term Changes

To get a better view of the long-term changes for the different elements, means for the different years were calculated (Table 3). The annual production in Kiirunavaara was also included, since the increased production could have increased elemental concentrations in the process water. Averaging the elemental concentrations over years removes the seasonal variation due to rain and melt water. However, variations between years due to different amounts of melt water and rain are still expected. A year where the process water is diluted by large amount of melt water and rain will on average have lower concentrations of elements (Granat 1990). It was also necessary to use the yearly mean values for the elements to compare them to production changes, since the production data were only available for whole years. A possible bias could come from using yearly mean concentrations and compare them to yearly production values. High productivity during a period where no sampling was performed combined with low productivity when sampling was performed could lead to artificially low elemental concentrations for that year. The duration of a possible effect on the recirculated process water from increased production was also unknown.

However, using the yearly means, the correlations between the different elements, conductivity, and production (Table 4) are a little lower but similar to the correlations in Table 2.

The PCA on the correlation matrix of the yearly mean long time variations at KVA001 (Fig. 5) shows that it is possible to explain almost 90% of the standardized variations of the elements with one factor. The second factor explains less than 10% and has a eigenvalue lover then 1, which is an indication that it could be pure noise. Also

Table 2 Correlations between the different elements and conductivity, 116 samples

	Conductivity	Ca	S	Na	Cl	Mg	K	Si	N	Sr
Conductivity	1.00	0.95	0.97	0.96	0.95	0.97	0.97	0.81	0.91	0.93
Ca	0.95	1.00	0.95	0.89	0.85	0.92	0.91	0.87	0.88	0.98
S	0.97	0.95	1.00	0.94	0.92	0.94	0.94	0.81	0.89	0.95
Na	0.96	0.89	0.94	1.00	0.96	0.94	0.98	0.70	0.85	0.88
Cl	0.95	0.85	0.92	0.96	1.00	0.94	0.97	0.69	0.87	0.82
Mg	0.97	0.92	0.94	0.94	0.94	1.00	0.96	0.79	0.92	0.89
K	0.97	0.91	0.94	0.98	0.97	0.96	1.00	0.73	0.87	0.88
Si	0.81	0.87	0.81	0.70	0.69	0.79	0.73	1.00	0.82	0.87
N	0.91	0.88	0.89	0.85	0.87	0.92	0.87	0.82	1.00	0.86
Sr	0.93	0.98	0.95	0.88	0.82	0.89	0.88	0.87	0.86	1.00

Table 3 Yearly mean values for production (kt) the sampled elements (mg/L) and conductivity (mS/m)

Year	Production	Conductivity	Ca	S	Na	Cl	Mg	K	Si	N	Sr	pH
1990	3,574	112										
1991	3,493	116										
1992	3,594	119	156	126	58	69	17	26	4.1	13.8	0.55	7.79
1993	3,711	117	153	126	56	73	16	25	3.7	10.8	0.55	7.86
1994	3,776	119	156	130	58	74	17	25	3.7	10.3	0.57	7.81
1995	6,445	132	160	139	68	89	20	29	4.2	12.2	0.58	7.84
1996	7,115	158	177	156	91	140	25	39	5.2	15.8	0.65	7.80
1997	7,718	157	176	159	91	148	25	38	5.3	15.9	0.61	7.80
1998	7,579	161	185	168	97	148	26	41	5.2	17.4	0.59	7.93
1999	5,825	142	185	163	92	118	23	37	7.3	14.0	0.65	7.89
2000	7,878	151	182	164	89	136	24	39	4.6	15.1	0.63	7.90
2001	6,908	140	161	141	80	124	20	35	3.7	12.8	0.55	7.91
2002	7,078	150	176	157	95	131	22	38	5.1	13.3	0.64	8.09
2003	7,540	183	208	190	119	175	26	47	5.6	16.5	0.74	8.10
2004	8,034	190	222	201	128	186	29	49	5.7	19.3	0.77	7.96
2005	8,571	166	200	175	102	150	25	43	5.8	18.2	0.69	
2006	8,618	183	228	212	114	165	27	48	6.3	19.8	0.72	
2007	8,788	181	230	216	110	157	26	45	6.2	17.5	0.78	

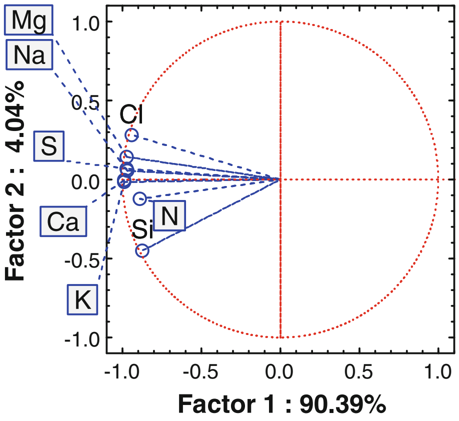

Fig. 4 The PCA with KVA001 data described in Table 1

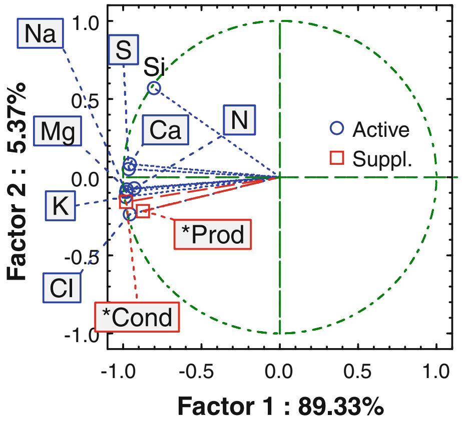

Fig. 5 The PCA over yearly mean data in KVA001 also showing production and conductivity as supplementary varibles

plotted in the figure are productivity and conductivity. Production lies almost directly on the first factors axis with a factor coordinate of −0.87, which means that it likely explains most of the elemental variation. This fits well with the high correlations in Table 4.

The high correlation between production and elemental concentrations also results in a high correlation between conductivity and production. To illustrate how the total ion concentration changes with production, electrical conductivity was plotted against production (Fig. 6). There is a significant correlation, which suggests that it may be possible to predict how a future production increase might affect water quality. Of the analyzed ions in this study, the ion with the largest known impact on flotation and pellet strength is Ca (Arol and Iwasaki 2003; Engesser 2003). This is mainly because Ca is a divalent ion and Ca concentrations in the process water are much higher than Mg concentrations throughout the system. A correlation coefficient only gives information about linear dependence while regression analyses makes it possible to estimate the mean value of the dependent variable when the independent variable is held fixed (in this case, the mean Ca concentration for a fixed production). Regression analyses also give information about how much of the dependent variables' variation could be explained by the independent variable.

A new pelletizing plant and a new process water system went on-line in 1995, so this was used as a start date to see

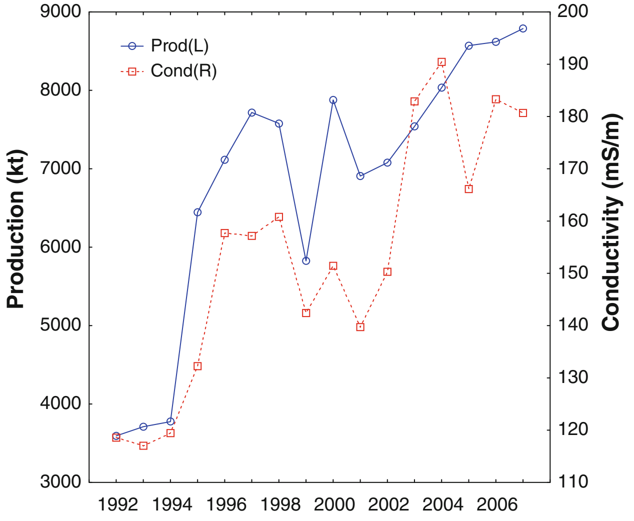

Fig. 6 Production (*blue*) and electrical conductivity (*red*) yearly mean data from Table 3

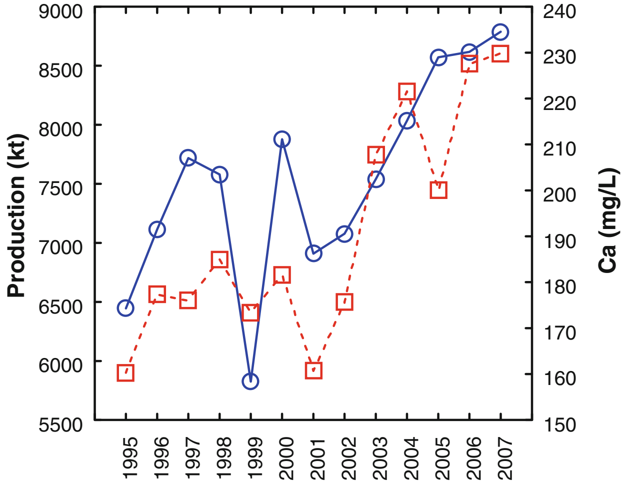

Fig. 7 Production (*blue*) and Ca (*red*), interpolated data for Ca year 1999

what effect future production increases could have on Ca concentrations in this system. During the sampling period, there were some years when no samples were taken during a certain month, and sometimes two samples were taken during 1 month. However, the distribution of samples during the years seems reasonable for all years except 1999. During that year, no samples were taken for Ca analysis after July. The data that were missing have been interpolated to correlate with the changes in conductivity in the new model to get a more realistic yearly mean. A regression model with production as an independent variable and Ca as a dependent variable was calculated.

This model gives an intercept constant at 23.2, which does not differ significantly from zero (p 0.56). Rock wells in the area have Ca concentrations around 15–30 mg/L (Aastrup et al. 1995). It seems realistic to think that this system would have some sort of base load of Ca concentration from which the regression should start. However, this cannot be concluded from the available data. The Ca concentration depends on variables besides the production volume. For example, a snow-rich winter or rainy summer would dilute the pond water. The water volume in the pond is regulated and differs from time to time, and a change in the used amount of additives in the process could also change the concentration. There is also the possible sampling bias discussed earlier. The variation of Ca and productivity over the years can be seen in Fig. 7.

Using the best available information, a regression model that explains about 60% (R^2 = .80, R^2 = .63, adjusted R^2 = .60, F(1,11) = 19 p) of the variation in Ca was calculated, as shown in Eq. 1. The constant 0.022 is statistically significant ($p < 0.01$)

$$\widehat{Ca}(\mathrm{mg/l}) = 23.2 + 0.022 \times \mathrm{prod} \tag{1}$$

In this model, the residuals can be assumed to be normally and independently distributed with an equal variance. A

Table 4 Correlations between elements, conductivity, and production data from Table 3, 13 samples

	Production	Conductivity	Ca	S	Na	Cl	Mg	K	Si	N	Sr
Production	1.00	0.85	0.70	0.79	0.83	0.90	0.89	0.88	0.46	0.75	0.60
Conductivity	0.85	1.00	0.95	0.97	0.98	0.98	0.97	0.98	0.59	0.89	0.88
Ca	0.70	0.95	1.00	0.99	0.96	0.91	0.91	0.94	0.69	0.87	0.95
S	0.79	0.97	0.99	1.00	0.98	0.95	0.95	0.97	0.69	0.87	0.92
Na	0.83	0.98	0.96	0.98	1.00	0.97	0.95	0.99	0.68	0.86	0.90
Cl	0.90	0.98	0.91	0.95	0.97	1.00	0.96	0.99	0.59	0.88	0.82
Mg	0.89	0.97	0.91	0.95	0.95	0.96	1.00	0.97	0.70	0.92	0.82
K	0.88	0.98	0.94	0.97	0.99	0.99	0.97	1.00	0.65	0.88	0.85
Si	0.46	0.59	0.69	0.69	0.68	0.59	0.70	0.65	1.00	0.59	0.67
N	0.75	0.89	0.87	0.87	0.86	0.88	0.92	0.88	0.59	1.00	0.72
Sr	0.60	0.88	0.95	0.92	0.90	0.82	0.82	0.85	0.67	0.72	1.00

Durbin–Watson test gives the d-value 1.9, which means that there probably is no autocorrelation in the model ($n = 13$, $p < 0.05$). The residuals indicates that there are no outliers (standard residuals between −2 and 2) (Montgomery 2005).

Since an increase in the production volume at the Kiirunavaara magnetite ore mine to 14,000 kt is being discussed, a predicted Ca concentration was calculated for that amount using Eq. 1. The predicted interval at a 95% prediction limit using Statistica (StatSoft 2008) is $253 < \mathrm{Ca} < 414$ mg/L. It is, however, very important to remember that this value lies outside the range of production that was used to derive the model and thus represents an extrapolation that would invalid if the system fails to behaves the same way outside the production values. Changes in the system or the mined ore would also affect the model. Still it would be wise to assume a wide range of concentrations, at least as high as this upper limit, in future research and projects. It is also worth remembering that the concentrations in the inner system are generally higher than in the clarifying pond, as discussed below.

Origin of Elements and Quality Variations in the Process Water

The results from the 04–06 sampling period in the mine and processing plants are listed in Table 5. Only 23 samples of 25 were used in the treatment of the data, since missing data from one or more sampling point would give the statistical analyses a disproportionate weight, since there are significant seasonal variations in the concentrations (Fig. 3). If, for example, one sampling point has more samples just before the snow melted, that sampling point would get an artificially high mean. At all of the sampling stations, Ca, S, Na, and Cl together accounted for more than 80% of the ions. Adding Mg, K, Si, and N increases this to more than 90%.

To compare the sampling stations in Table 5 to the KVA 001 sampling station, the number of samples was reduced to 14 due to missing data. This had no major impact on the mean values. The largest change was 7% for Si in KVA 116, and most changes were less than 3%. Looking at the mean values of the different elements at the different stations, it is evident that most of the Ca, S, N, and Si in the inner system comes from the mine water. For the other elements, the main sources has its origin in the process chain. The sources in the process chain could be finely milled minerals and fluid inclusions. Fluid inclusions with high concentration of Na and Cl ions have been found in other similar magnetite apatite ores (Broman et al. 1999), and were suggested by Lundkvist (1998) as a possible source at Kiirunavaara. In 2009, quartz-carbonate-(magnetite-titanite) veins which cut the ore body at Kiirunavaara where studied by Gleeson and Smith (2009). Fluid inclusions with NaCl concentrations between 30 and 40 wt% were found.

Table 5 Mean, minimum, and maximum values for the different elements in (mg/L) at the mine and different processing plants. Note to printer: the spacing on this and Table 7 is arbitrary; feel free to adjust it. It was just meant to indicate that the table could/should be divided into columns, rather than having it all in one narrow column

	Mean	Minimum	Maximum	Mean	Minimum	Maximum
KVA 114 sorting plant				*KVA 120 pelletizing plant*		
Ca	232.2	181	287	241	196	305
S	198.2	146	254	221.2	169	294
Na	98	66	153	128.8	99.1	163
Cl	133.3	91	180	188.7	140	290
Mg	24.7	18.3	31.1	30.8	24.3	37.7
K	40.7	27.8	64	54.3	41.2	69.3
Si	7.5	4.3	11.6	9.5	6.4	13
N	22.9	16	35	24.7	17	33
KVA 116 concentrating plant				*KVA 33 mine*		
Ca	275.7	206	366	241.6	202	268
S	261.3	165	375	178.3	145	203
Na	196.6	69.5	277	24.2	20.7	29.9
Cl	303.9	220	440	17.2	13	24
Mg	37.9	19.6	49.4	12	10.3	17.8
K	82.4	29.8	112	7.1	5.5	9.4
Si	10.5	6.2	15.5	8.7	7.1	14
N	33.7	22	54	18.6	13	30
KVA 118 concentrating plant						
Ca	248.5	199	332			
S	233.3	174	335			
Na	143.1	110	181			
Cl	208.2	160	260			
Mg	32.8	25.2	41.6			
K	60.3	46.9	76.3			
Si	10.2	7	13.9			
N	27	19	34			

At KVA001, all elements have lower mean concentrations than in the process system. This could be due to precipitation, surface reactions, or dilution. A dilution effect should affect all elements. Since all elements in KVA 001 have lower values than the mean in the process chain, dilution by rain and melt water is at least partly responsible for the lower values at KVA 001. If precipitation or surface reactions were the main reason behind the lower values at KVA 001, changes between the different elements should be clear. For example calcite has been oversaturated in the process system for many years (Westerstrand and Ohlander 2010). However, calcite precipitation cannot be the main reason for the lower elemental concentrations at KVA 001 since it should not affect, for example, Na concentrations.

Table 6 Correlation for Ca, S, and N concentrations at the different sampling stations

	KVA001 Ca	KV114 Ca	KVA116 Ca	KVA118 Ca	KVA120 Ca	KVA33 Ca
KVA001 Ca	1.00	0.94	0.91	0.93	0.94	0.80
KVA114 Ca	0.94	1.00	0.88	0.92	0.93	0.78
KVA116 Ca	0.91	0.88	1.00	0.96	0.94	0.71
KVA118 Ca	0.93	0.92	0.96	1.00	0.99	0.70
KVA120 Ca	0.94	0.93	0.94	0.99	1.00	0.74
KVA33 Ca	0.80	0.78	0.71	0.70	0.74	1.00
	KVA001 S	KVA114 S	KVA116 S	KVA118 S	KVA120 S	KVA33 S
KVA001 S	1.00	0.91	0.93	0.92	0.94	0.76
KVA114 S	0.91	1.00	0.82	0.87	0.91	0.77
KVA116 S	0.93	0.82	1.00	0.97	0.95	0.68
KVA118 S	0.92	0.87	0.97	1.00	0.98	0.66
KVA120 S	0.94	0.91	0.95	0.98	1.00	0.73
KVA33 S	0.76	0.77	0.68	0.66	0.73	1.00
	KVA001 N	KVA114 N	KVA116 N	KVA118 N	KVA120 N	KVA33 N
KVA001 N	1.00	0.92	0.90	0.84	0.80	-0.35
KVA114 N	0.92	1.00	0.91	0.91	0.87	-0.14
KVA116 N	0.90	0.91	1.00	0.85	0.87	-0.29
KVA118 N	0.84	0.91	0.85	1.00	0.95	0.08
KVA120 N	0.80	0.87	0.87	0.95	1.00	0.12
KVA33 N	−0.35	−0.14	−0.29	0.08	0.12	1.00

An analysis of the process water with the computer program PHREEQC showed that calcite is the most probable mineral to precipitate, but no evidence for this actually happening were found (Westerstrand and Ohlander 2010). This means that it is likely that the ponds help to lower the concentration of ions in the process by diluting the process water. Both the PCA (Fig. 4) and conductivity variations (Fig. 3) support a dilution effect at KVA 001. Since KVA 001 has a large drainage area, this is where most of the dilution of the process water would be expected. It therefore is probable that the recirculation of process water in the different plants leads to higher concentrations of the different elements.

Table 6 shows Ca, S, and N correlations in the system, and the proportion of common variation in the specific element concentrations between the different sampling points. For Ca and S, there is a strong correlation, statistically significant at a 95% significance level, throughout the entire system. The strong correlations throughout the system show that the process water in the process chain is affected by concentration changes in the mine water. The close relationship between S and Ca and a molar ratio slightly above one led Lundkvist (1998) to suggest that pyrite, calcite, anhydrite, and gypsum weathering could be the source of these elements. Both pyrite and calcite were found in the ore by Bergman et al. (2001) and Parák (1975), and pyrite is easily oxidized, which lowers, pH, while calcite is a well known buffering agent. The new data support this conclusion, since the ratio still lies around the same value. Most of the nitrogen in the process plants, mainly occurring as nitrate, comes from KVA 33 (the mine water), but nitrogen concentrations show a different variation at KVA 33 than in the rest of the system (a low correlation, not statistically significant at 95% level). This means that the mine water is not the major source of nitrogen variation in the process water system, and that the variability in nitrogen has to come from some other part of the system. Lundkvist (1998) concluded that undetonated explosives used in the mine could be the main source of N in the system. This is a reasonable explanation for the data shown here as well. Explosives spill out in the mine where the detonations occur, but some, apparently, are washed off of the ore during processing. However, it is not known what controls how much goes directly into the mine water and how much is washed out during processing.

Comparing the 2004–2006 Data to that Obtained by Lundkvist (1998) during 1994–1996

To get comparable data between the two sets, all samples that were not taken close in time (a few days) to the

Table 7 Descriptive values for the different elements from Lundkvist 1998, the samples were taken between 1994 and 1996

	Mean	Minimum	Maximum	Mean	Minimum	Maximum
KVA 33				*KVA 116*		
Cl	19.4	16.3	26.7	218.5	82.7	280
Ca	201.2	194	210	192.6	145	242
K	5.9	4.6	7.3	59.8	33.6	71.1
Mg	10.1	9.3	11	27.4	19.7	36.3
Na	20.5	19	23.8	136.9	77.3	167
S	143.2	136	157	164.2	128	191
Si	7.5	7.2	7.7	4.3	3	6.1
N	14.4	10.2	18.6	23	12.2	30.6
KVA 114				*KVA 118*		
Cl	100.1	67.9	137	123	109	138
Ca	180	156	224	177.2	157	224
K	25.6	20.3	32.4	42	34.5	57.6
Mg	19.6	16.7	24.2	25.9	22	33.5
Na	63.1	50.4	82.3	99.1	79.3	141
S	144.8	128	169	152	135	178
Si	5.3	2.8	7.9	7.9	6.4	9.9
N	17.3	13	19.7	19	16	21.7

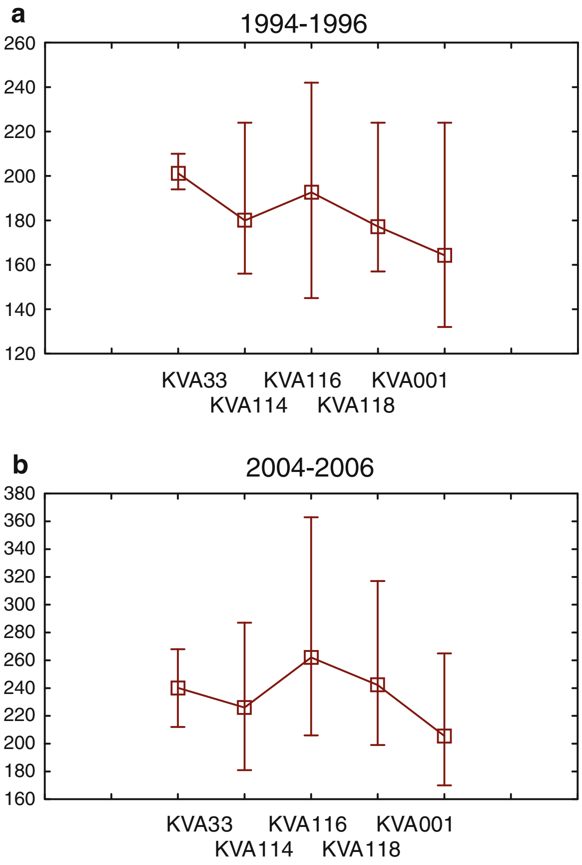

Fig. 8 Mean, maximum and minimum values for Ca (mg/L) at the different sampling stations during 1994–1996 and 2004–2006

corresponding data in the other group were deleted, leaving only 5 samples in each group. Lundkvist's data is shown in Table 7 as periodic means. All means are higher for the 04–06 period except for Cl in the mine water at KVA 33 (Fig. 8). The reason for the Cl exception is not known. The increased concentrations in the mine water at KVA 33 might have many explanations, such as increased weathering due to, for example, changes in groundwater levels around the mine or inflow of process water and water from waste rock piles into the groundwater. However, the concentrations in the process water system are generally higher for all elements. This is seen most clearly for Ca, which during 94–96 had a higher mean concentration in the mine than in the process system (Fig. 8). This supports the suggestion that both production increase and recirculation of water could increase elemental concentrations in the process water at mine sites.

Given the few samples and large seasonal variations, no test for statistical differences was possible. Despite this, it seems clear that production increases affected the concentrations in the entire system, which could be expected from the results of the long time series shown in Fig. 3.

Conclusions

The dissolved elemental concentrations in the process water system at Kiirunavaara are dominated by Ca, S, Na, and Cl. In the clarifying pond, Ca has the highest mean concentration, 183 mg/L, and the highest maximum concentration, 303 mg/L, followed by S, 162 and 292 mg/L, Cl, 132 and 250 mg/L, and Na, 88 and 172 mg/L. These elements account for over 80% of the concentration at all sampling stations. The increase in production has resulted in an increase in the concentration of Ca, S, Na, Cl, Si, N, K, and Mg at all sampling points throughout the process. It is also evident that the increase in elemental concentrations in the inner process system was higher than in the rest of the system. There is a distinct seasonal variation in elemental concentrations, reflecting the effect of dilution by snow melt and the rainy season, mainly through the open pond system.

It is probable that the high concentrations of Ca and S originate from sulfide oxidation and calcite buffering in the drainage area, and that crushing and milling during the processing releases Na and Cl, from fluid inclusions in the ore minerals, with subsequent increased concentrations of these elements in the process water. It is also probable that most of the elevated N concentrations in the process water come from undetonated explosives. A combination of increased recirculation and increased production increases elemental concentrations throughout the process system.

A simple regression model was used to predict future Ca concentrations due to further production increases. Even though the model has some uncertainties, Ca concentrations of about 400 mg/L should be considered throughout the process chain in future planning if the planned production increase proceeds at the Kiirunavaara magnetite ore mine.

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